

# UNCLASSIFIED

AD NUMBER
AD406936
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; 31 DEC 1962. Other requests shall be referred to Office of Naval REsearch, Washington, DC.
AUTHORITY
ONR

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED  
AND CLEARED FOR PUBLIC RELEASE  
UNDER DOD DIRECTIVE 5200.20 AND  
NO RESTRICTIONS ARE IMPOSED UPON  
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

UNCLASSIFIED

AD 406 936 \_

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



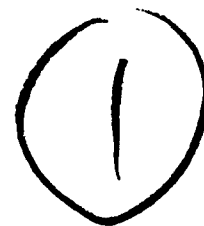
UNCLASSIFIED

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

406936

ORIGINAL CONTAINS COLOR PLATES: ALL DDC  
REPRODUCTIONS WILL BE IN BLACK AND WHITE:  
ORIGINAL MAY BE SEEN IN DDC HEADQUARTERS

710



NOT SUITABLE FOR RELEASE TO OTS

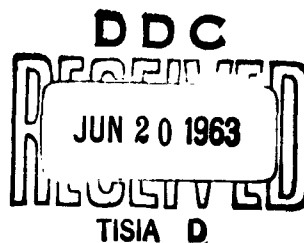
AD No. \_\_\_\_\_

DDC FILE COPY

406 936

*Seab-2*

EASTMAN KODAK COMPANY  
APPARATUS AND OPTICAL DIVISION



NO OTS

4 NA 5280800  
7 + 8 NA

(21)

ORIGINAL: ALL LDC  
REPRODUCTIONS MUST BE IN BLACK AND WHITE.  
ORIGINAL MAY BE KEPT IN LDC HEADQUARTERS.

(15) LASER MATERIAL STUDY.  
Contract Nonr - 383400  
Semi-Annual Technical Report  
July 1 - Dec. 31, 1962  
(16) ARPA NO. 306462  
Project Code Number 7300

11 31 Dec 62,  
12 45p. 13 NA  
14 NA 17 18 +  
11 NA 20 1  
21 10 46

Prepared by  
Eastman Kodak Company  
Apparatus and Optical Division  
Rochester 4, New York

For  
Advanced Research Projects Agency  
and  
Office of Naval Research  
Department of Navy

Prepared by:

Paul B. Mauer  
Paul Mauer  
Research and Engineering

Approved by:

Wayne M. Kusick  
Wayne McKusick, Project Manager  
Research and Engineering

Kod

## TABLE OF CONTENTS

	<u>Page</u>
List of Illustrations	11
Introduction	1
SECTION I	
General Description	2
A. Optical Absorption and Fluorescence Lifetime of Neodymium in Glass	3
B. Observations on Laser Action	6
C. Other Rare-Earth Activated Glasses	8
SECTION II	
Experimental	10
A. Absorption Spectra	11
B. Fluorescence Spectra	18
C. Fluorescence Decay	25
D. Decay vs. Concentration	27
E. Decay vs. Time	30
F. Laser Action	34
G. Absorption and Fluorescence Measurements on Various Glass Systems	39
H. Glass Optical Quality	43

# LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
A-1	Transmittance: 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In EK-110 Glass Thickness - 5.6mm	12
A-2	Transmittance: 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In K-Ba-Silicate Glass Thickness - 13.8mm	13
A-3	Transmittance: 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In La-Ba-Silicate Glass Thickness - 3.9mm	14
A-4	Transmittance: 1 Wt. Percent $\text{Sm}_2\text{O}_3$ In La-Ba-Borate Glass Thickness - 16.9mm	15
A-5	Transmittance: 1/3 Wt. Percent $\text{Yb}_2\text{O}_3$ In La-Ba-Borate Glass Thickness - 18.8mm	16
A-6	Transmittance: 1 Wt. Percent $\text{Tb}_2\text{O}_3$ In Na-Borate Glass Thickness - 3.7mm	17
B-1	Fluorescence Emission from 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In La-Ba-Borate Glass (Amplifier gain 4X that used for B-2 and B-3)	19
B-2	Fluorescence Emission from 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In La-Ba-Silicate Glass	20
B-3	Fluorescence Emission from 1 Wt. Percent $\text{Nd}_2\text{O}_3$ In K-Ba-Silicate Glass	21
B-4	Fluorescence Emission from 1 Wt. Percent $\text{Sm}_2\text{O}_3$ In La-Ba-Borate Glass	22
B-5	Fluorescence Emission from 1/3 Wt. Percent $\text{Yb}_2\text{O}_3$ In La-Ba-Borate Glass	23
B-6	Fluorescence Emission from 1 Wt. Percent $\text{Tb}_2\text{O}_3$ In Na-Borate Glass	24
C-1	Fluorescence Decay Curve for 1/3 Wt. Percent $\text{Sm}_2\text{O}_3$ in La-Ba-Borate Glass 1 Millisecond/Division	26
C-2	Fluorescence Decay Curve for 1/3 Wt. Percent $\text{Yb}_2\text{O}_3$ in La-Ba-Borate Glass 0.5 Millisecond/Division	26



<u>Figure</u>		<u>Page</u>
C-3	Fluorescence Decay Curve for 1 Wt. Percent $Tb_2O_3$ in Na-Borate Glass 2 Milliseconds/Division	26
D-1	Lifetime as a Function of Concentration for $Nd_2O_3$ in La-Ba-Borate Glass	28
D-2	Lifetime as a Function of Concentration for $Nd_2O_3$ in La-Ba-Borate Glass	29
E-1	Length of Time for Fluorescence to Decay A Factor of 3 as a Function of Time for 1 Wt. Percent $Nd_2O_3$ in EK-110 Glass	31
E-2	Length of Time for Fluorescence to Decay A Factor of 3 as a Function of Time for 1 Wt. Percent $Nd_2O_3$ in K-Ba-Silicate Glass	32
E-3	Length of Time for Fluorescence to Decay A Factor of 3 as a Function of Time for 1 Wt. Percent $Nd_2O_3$ in La-Ba-Silicate Glass	33
F-1	Typical Nature of Laser Output as a Function of Time for 1 Wt. Percent $Nd_2O_3$ in Borate Glass - Time Scale 0.2 Milliseconds/Division (Sweep right to left) Input power 144 joules	36
F-2	Typical Nature of Laser Output as a Function of Time for 2 Wt. Percent $Nd_2O_3$ in Silicate Glass - Time Scale 0.2 Milliseconds/Division (Sweep right to left) Input power 530 joules	36
F-3	Output near Threshold of Borate Glass with Constant Pump Light Time Scale 0.2 Millisecond/Division (Sweep left to right) Input power 196 joules	36
F-4	Output near Threshold of Silicate Glass with Constant Pump Light Time Scale 0.2 Milliseconds/Division (Sweep left to right) Input power 525 joules	37
F-5	Output of Q-spoiled 3 Wt. Percent $Nd_2O_3$ EK-110 Glass - Time Scale 50 Microseconds/Division (Sweep left to right)	37
F-6	Power Output of 1 Wt. Percent $Nd_2O_3$ in EK-110 Glass Rod, 2 Inches long, 1/4 inch in Diameter Energy Measured with TRG Laser-Rater	38

<u>Figure</u>		<u>Page</u>
H-1	EK-110 Glass with 1 Wt. Percent $\text{Nd}_2\text{O}_3$ 2 Inches Thick	45
H-2	EK-110 Glass with 1 Wt. Percent $\text{Nd}_2\text{O}_3$ 2 Inches Thick	45
H-3	EK-497 Glass with 1 Wt. Percent $\text{Nd}_2\text{O}_3$ 2 Inches Thick	45

## Introduction

The work ~~initiated under this contract~~ is aimed at a better understanding of the mechanisms involved in stimulated emission in solid materials, to provide a basis for improvements in the efficiency of laser materials.

Although much of the experimental work has centered around the neodymium-doped borate glasses, other ions and host materials ~~have been~~ studied. Neodymium-doped borate glass rods ~~have been~~ fabricated in various sizes and laser action studied in order to direct basic study effort towards increased efficiency in practical configurations.

This first technical report reflects the exploratory nature of the initial effort in its format and content. It is presented as a fairly complete record of raw data with current observations and reflections on the significance of these data. ~~The final report will attempt to go further in the direction of correlation between observations and specific conclusions.~~

## SECTION I

### General Description

Three aspects of improving glass laser materials have been considered and are discussed in detail, but in a qualitative manner, in this section.

They are:

- A. Optical Absorption and Fluorescence Lifetime of Neodymium in Glass
- B. Observations on Laser Action
- C. Other Rare-Earth Activated Glasses

#### A. Optical Absorption and Fluorescence Lifetime of Neodymium in Glass

Since the inner 4f electric dipole transitions are forbidden by quantum mechanical selection rules, only ions whose energy states are perturbed by the surrounding field will exhibit absorption or emission of electromagnetic energy (by forced electric dipole transitions).<sup>1</sup> Possible exceptions are the magnetic dipole transitions occasionally observed in rare-earths; for example, the  ${}^7F_0 \rightarrow {}^5D_1$  of europium +3 in europium ethyl sulfate.<sup>2</sup> However, magnetic dipole transitions are characteristically very weak, and are generally of the same order of strength as forced electric dipole transitions.

Since the transition probabilities are strongly dependent on the type and strength of perturbing fields, large differences should be observed in absorption cross sections and fluorescence lifetimes for rare-earth ions in different matrices.<sup>3</sup> There are two important features in the surrounding field; its strength and its symmetry. Both contribute to the relaxation of selection rules to allow inner 4f transitions. The field strength is largely determined by ionic charge radius and the charge on neighboring ions.<sup>4</sup> Since the glasses we have studied are primarily oxide systems, and the neodymium ion is comparatively large, the field strength probably does not change much from one glass to another. The symmetry, however, may be drastically influenced, for example, by the substitution of a metal ion for one of the neighboring oxygen ions. A possible case in point is the nearly full order of magnitude change of absorption cross section between neodymium in potassium-barium silicate and lanthanum-barium silicate

- 
1. J. H. van Vleck, J. Phys. Chem. 41, 67 (1937) Broer, Gorter and Hoogschagen, Physica 11, 231 (1945).
  2. Sayre and Freed, J. Chem. Phys. 24, 1213 (1956).
  3. W. Low, Phys. Rev. 105, 801 (1957), Towns, Quantum Electronics, Columbia Univ. Press (1960) p. 421., Keating and Drickamer, J. Chem. Phys. 34, 143 (1961), Ballhausen and Liehr. J. Mol. Spectroscopy 2, 342 (1958).
  4. Bates and Douglas, J. Soc. Glass Tech. 43, 289T (1959), Moffitt and Ballhausen, Ann. Rev. Phys. Chem. 7, 107 (1956).

glasses. The replacement of a neighboring monovalent, highly polarizable ion such as potassium, by the trivalent lanthanum ion, could easily have a pronounced effect on the field symmetry.

Another problem associated with individual ions in glass is that they are all in different surround environments.<sup>5</sup> It is possible that a small percentage of the ions, in a highly asymmetric field, could account for a high percentage of the absorption and fluorescence. The decay of fluorescence would not be expected to follow a simple exponential law, and the absorption constants at high excitation levels would be non-linear. We have observed non-exponential fluorescence decays and find that over a limited range the decay rate appears to decrease linearly with time.

One of the major considerations in fluorescence is the existence of competing mechanisms to dissipate the stored energy of the excited state of the ion. ".....Energy may be dissipated by an internal conversion to molecular or crystal lattice vibrations. This latter transfer is due to the coupling of the excited atom to its surrounds through the crystal field."<sup>6</sup> The efficiency of this process is increased as the active ion concentration is increased. A model for this so-called "concentration quenching" is that the rare-earth ions are coupled energetically by the forced motion of one intervening oxygen atom whose energy can be dissipated by exciting lattice vibrations.<sup>7</sup> Just how the frequency is degenerated into one of the allowed modes of the lattice is not understood. However, the higher the rare-earth ion concentration, the greater the probability of coupling between ions via forced oscillation of an intervening matrix ion.

- 
5. W. A. Weyl, J. Appl. Phys. 17, 628 (1946), Weyl and Marboe, The Glass Industry, 42, 76 (1961).
  6. E. H. Carlson, John Hopkins Spectroscopic Report No. 18 (1960), see p. 31, Hall and Dieke, J. Optical Soc, Am. 47, 1092 (1957), Carlson and Dieke, J. Chem. Phys. 29, 229 (1958).
  7. Van Uitert, Linarcs, Soden and Ballman, J. Chem, Phys. 36, 702 (1962).

A more serious quenching of fluorescence occurs when there exists in the matrix an impurity ion which has strongly permitted transitions energetically matched to the excitation energy of the rare-earth. Although the concentration of such an impurity is very low, its influence would be present over a large radius since its transitions may be many orders of magnitude more probable than those in the rare-earth ions. The energy is probably lost in the process of transfer from rare-earth ion to impurity ion via forced motion of intermediate matrix ions.

A third possibility is that the matrix itself may possess high order vibrational harmonics whose energy may fall in the range of energy transitions of the rare-earth ion. A case of primary interest is our observation that glasses which have boron oxide as a major constituent (so called "borate" glasses) show more rapid fluorescence decay than would be expected from the strength of the absorption bands. The assumption is that the strength of absorption, averaged over a number of unrelated bands, is an indicator of the degree of perturbation of the electronic wave functions in the  $4f$  levels. Thus, if there were no other energy loss mechanisms, the absorption cross section and the fluorescence lifetime should be reciprocally related quantities. The product of fluorescence lifetime and absorption cross section should serve as a figure of merit in evaluating the efficiencies of the fluorescence process.

It should be pointed out that when stimulated emission becomes the predominant loss mechanism, other competing mechanisms become less significant since the stimulated emission occurs at such a rapid rate. Once threshold for laser action is achieved, the efficiency of energy conversion from pump light to laser output may be quite similar for materials having widely differing figures of merit based on fluorescence efficiency alone.

## B. Observations on Laser Action

One of the more puzzling aspects of our work has been the consistent tendency of borate glass systems to exhibit lower thresholds than silicates, although the latter have much higher fluorescent efficiency and longer storage lifetime. In an effort to eliminate the time variation of pump light, we constructed a lumped constant, 8-element, delay line to supply the flash tubes. The light output was roughly constant for about 1200 microseconds.

Even under these conditions, the threshold for laser action was more than a factor of 2 lower for borate glass than for silicate. The initiation of action was somewhat earlier for the short lifetime borate glass.

Our current speculation is that the scatter inherent in the silicate glass must account for the observed differences. The scatter might be explained if one assumed that the rare-earth oxide is not as readily soluble in silicate as in borate glasses and localized areas of varying refractive index result which produce scattering loss.

Another feature of the laser action is the type of spiking observed in the output as a function of time. The silicate glass has a tendency to pulse and return to zero output before pulsing again in a somewhat irregular pattern. The shorter-lifetime borate glass seems to have a steady state component of output at energies only slightly above threshold, and have oscillations of output which are fairly regular about the steady state value.

The laser output power seems to rise linearly with input at pumping levels substantially higher than threshold for the borate glass. Our pump source did not have the energy required to get similar data for the silicate glass.

We have only done a preliminary experiment to illustrate Q-spoiling in the borate glass. A rotating prism was used and a rod with a high reflection coating on one end and a low reflection coating on the other. Output was observed about 150 microseconds after initiation of the pumping light. No estimate of pulse width or peak power has been made.



A twelve inch long, roof prism ended rod has been submitted to the General Engineering Laboratory of the General Electric Company in Schenectady. Dr J. Chernoch of that laboratory has reported to us by private communication that output powers in the 20 - 40 joule range have been achieved with a beam divergence of less than  $1/4$  degree. In terms of brightness, this compares very favorably with silicate glass outputs where the energy may be spread into several degrees.

### C. Other Rare-Earth Activated Glasses

We have evidence in borate glass, of its good optical quality and ability to accommodate rare-earth ions. The disadvantage for neodymium is the presence of a high order optical phonon mode which drains energy from the excited neodymium ion.

Several other rare-earth ions which have larger gaps in their energy level spectrum should not have their fluorescence quenched by borate phonons. Three of these have been studied for absorption and fluorescence, but no laser action has been observed in any in our laboratory.

Samarium in low concentrations appears to have a lifetime approaching 3 milliseconds. Pumping is difficult, however, because of the comparative weakness of the available absorption bands. If a pump source were available with a high concentration of output at 400 millimicrons, this problem could perhaps be solved. Possible coupling of divalent europium fluorescence has been considered but not as yet been attempted.

Terbium exhibits a powerful absorption band between 190 and 230 millimicrons. This presumably is a  $4f \rightarrow 5d$  transition since the inner  $4f$  transitions are very weak and difficult to observe. The pumping of this system is also difficult since the lamp walls begin to absorb at short wavelengths. The heavy-metal borates which we have used for base glasses all absorb at wavelengths less than 300 millimicrons. We have tried sodium and lithium borates as base glasses and observed strong terbium fluorescence at 550 millimicrons with a 3 millisecond time constant.

Ytterbium fluoresces very efficiently in our lanthanum barium borate base glass with a lifetime of about 1.1 milliseconds. The problem with ytterbium is that its fluorescence returns the ion very close in energy to the ground state condition and extremely low temperature operation is indicated.

Terbium has the advantage over ytterbium in that its terminal state is as high above the ground state as is that of neodymium. Samarium has two equally probable terminal states for fluorescence. The wavelengths of the samarium emission corresponding to these are 600 and 650 millimicrons. Since the 650 millimicron emission returns the ion to a higher energy, comparable to the terminal state in neodymium, it would be the most likely to evidence laser action.

## SECTION II

### Experimental

In this section the results of some measurements on absorption, fluorescence and laser action of rare-earth doped glasses are reported. The constants associated with absorption and fluorescence of neodymium in several borate, silicate, and phosphate glass systems are presented in tabular form.

The various figures which follow are accompanied by details of the measurement involved. They are divided into eight main categories:

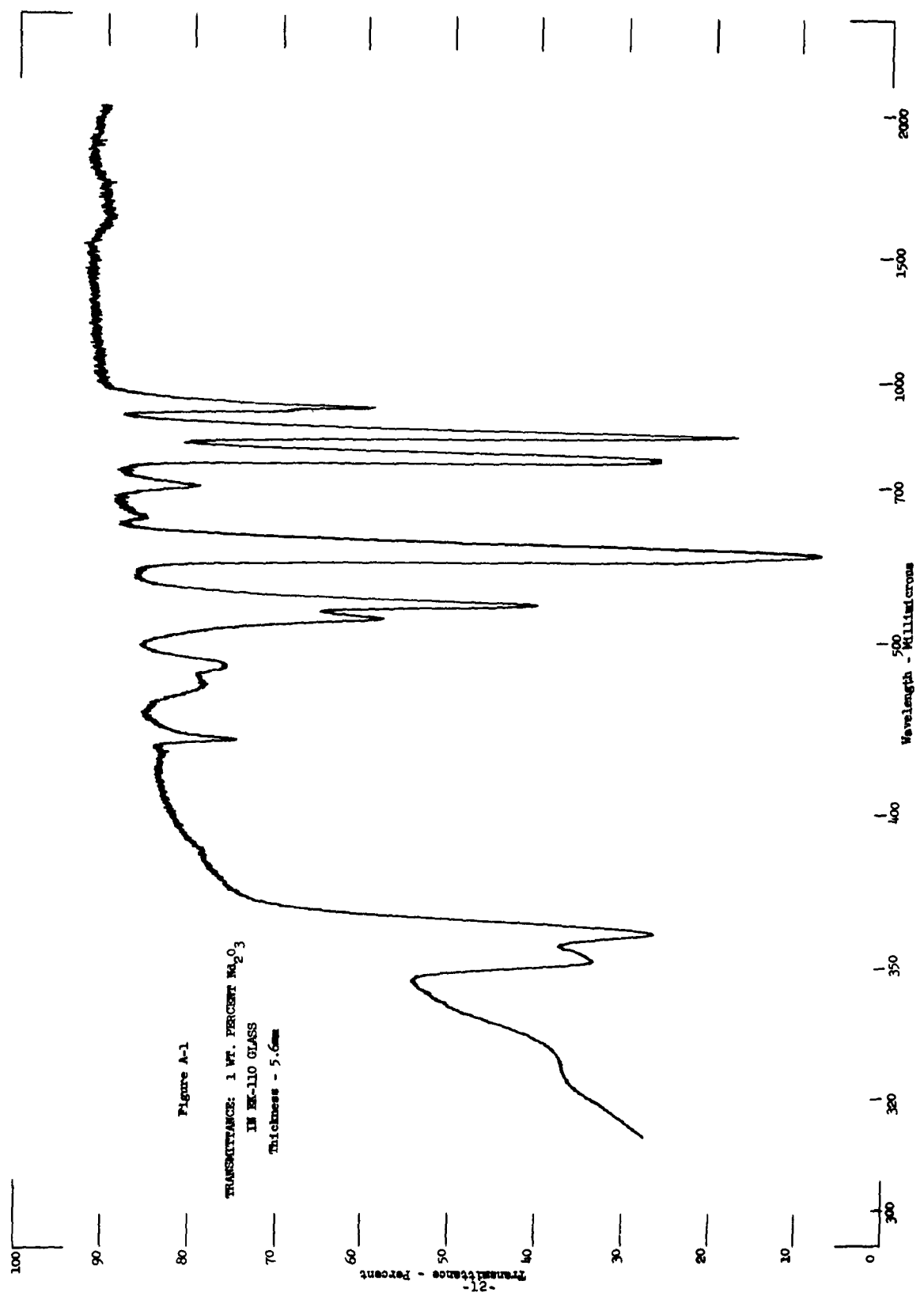
- A. Absorption Spectra
- B. Fluorescence Spectra
- C. Fluorescence Decay
- D. Decay vs. Concentration
- E. Decay vs. Time
- F. Laser Activity
- G. Absorption and Fluorescence Measurements on Various  
Glass Systems
- H. Glass Optical Quality

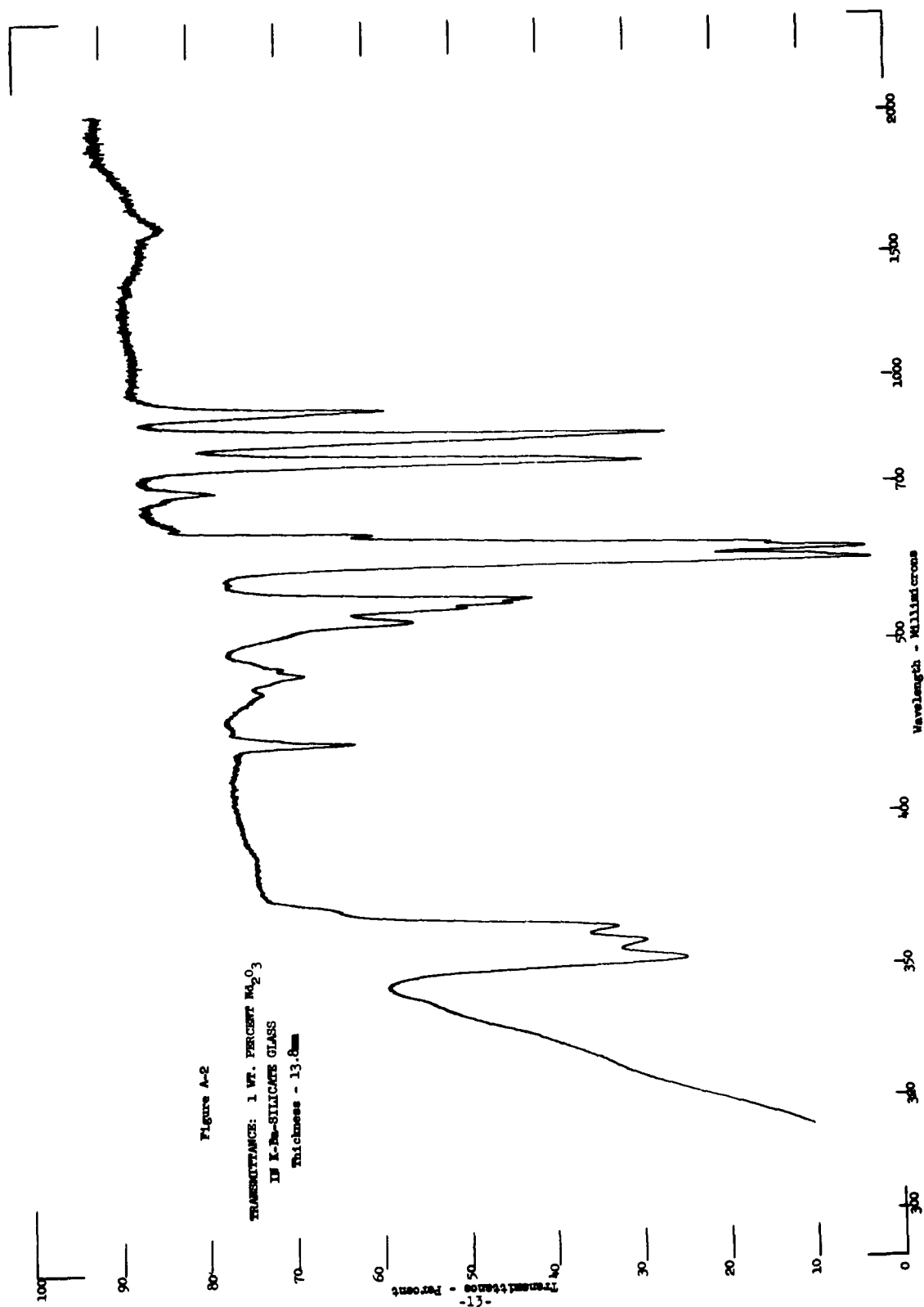
#### A. Absorption Spectra

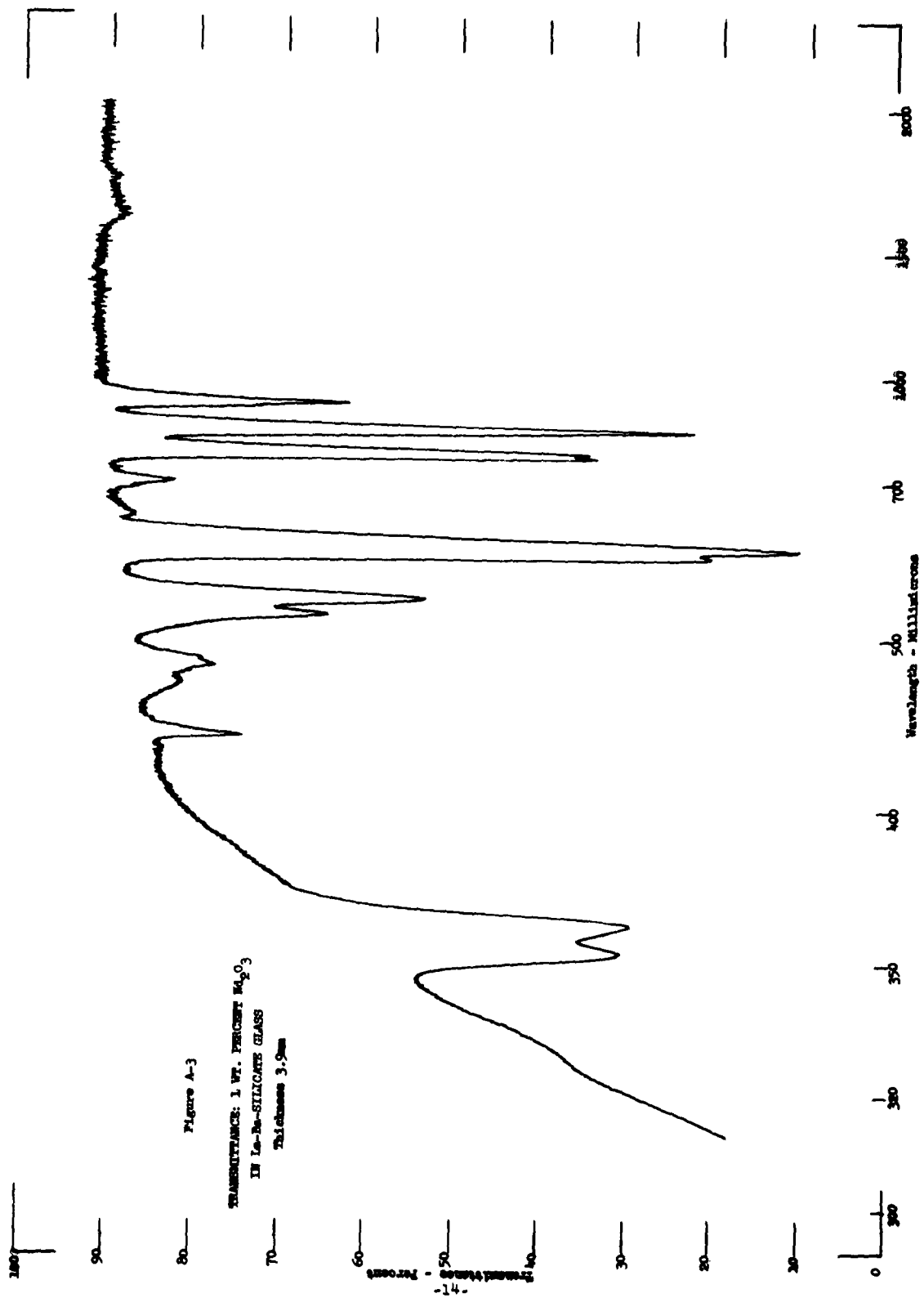
The curves included for neodymium absorption are representative of the many which have been made in preparing the tabular data. Also included are data on samarium, ytterbium, terbium and the special Na-borate glass used as host for the terbium.

The curves were all made on a Beckman DK-2 spectrophotometer. Detectors and sources were changed to optimize performance in various parts of the spectrum. Some of the samples were of poor optical quality and showed reduced short wavelength transmission due to scattering.

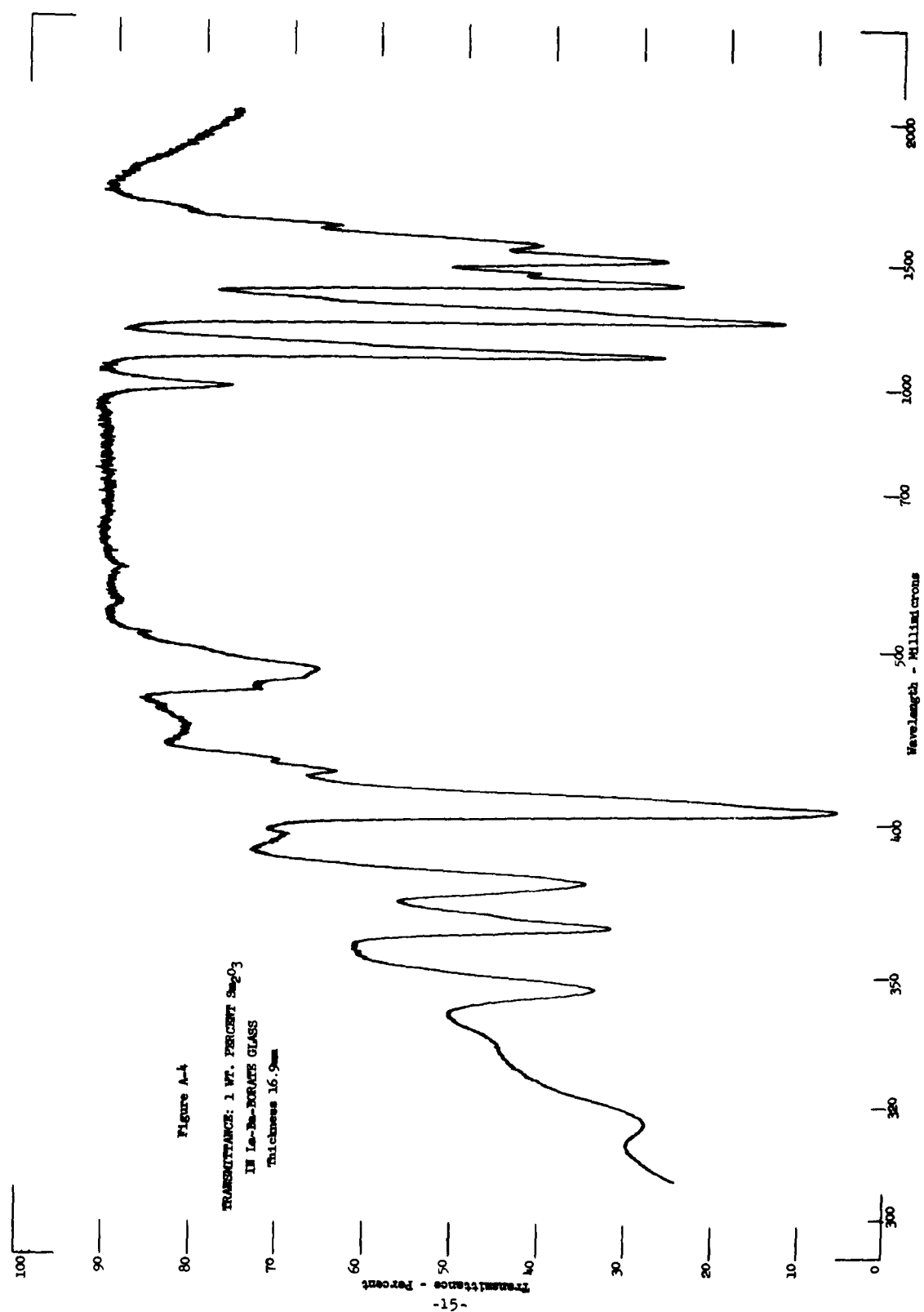
Samples have been chosen in such a way as to approximately normalize absorption strengths. To do this it was necessary to make the K-Ba-Silicate much thicker than the La-Ba-Silicate or the EK-110 Borate.

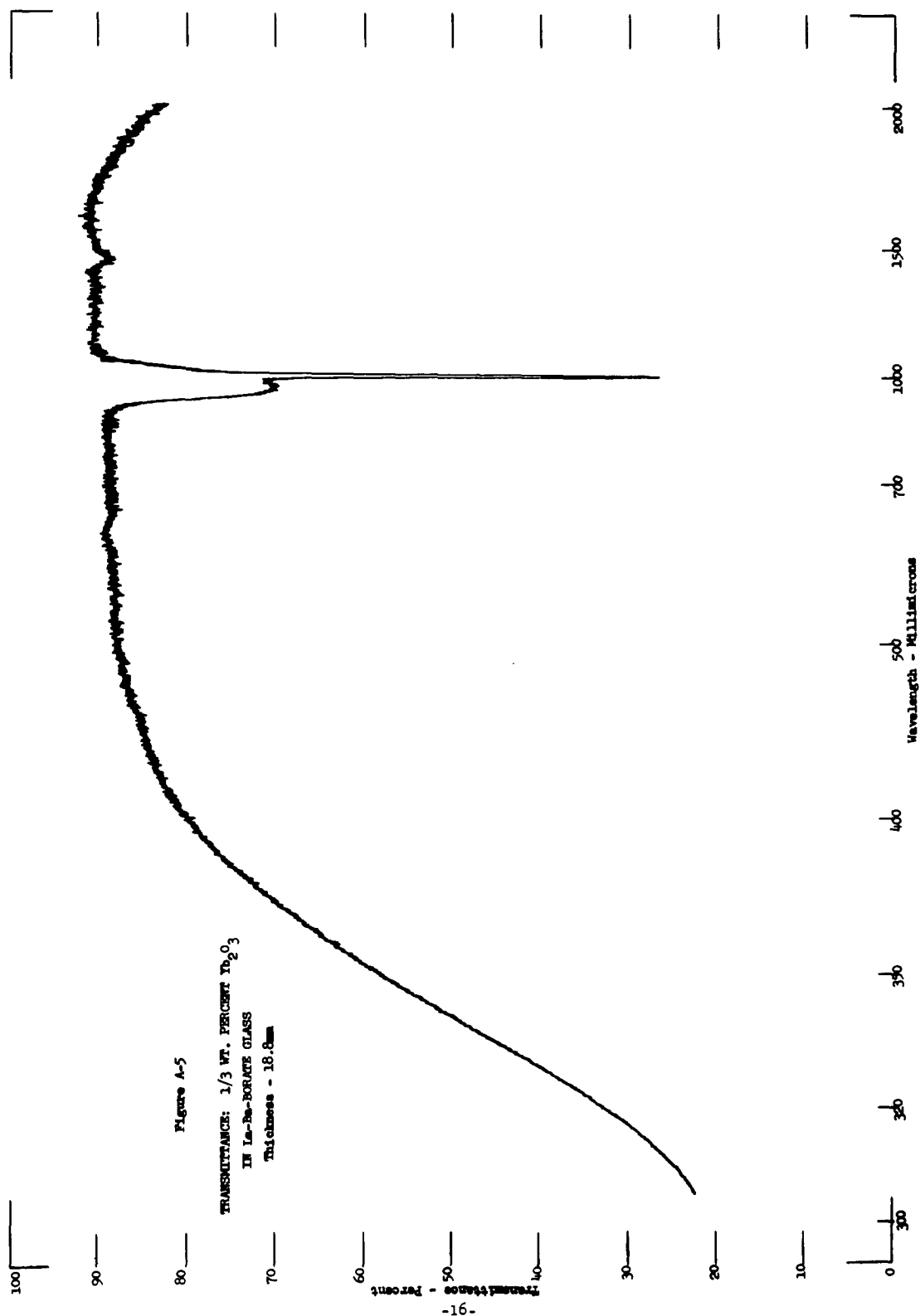


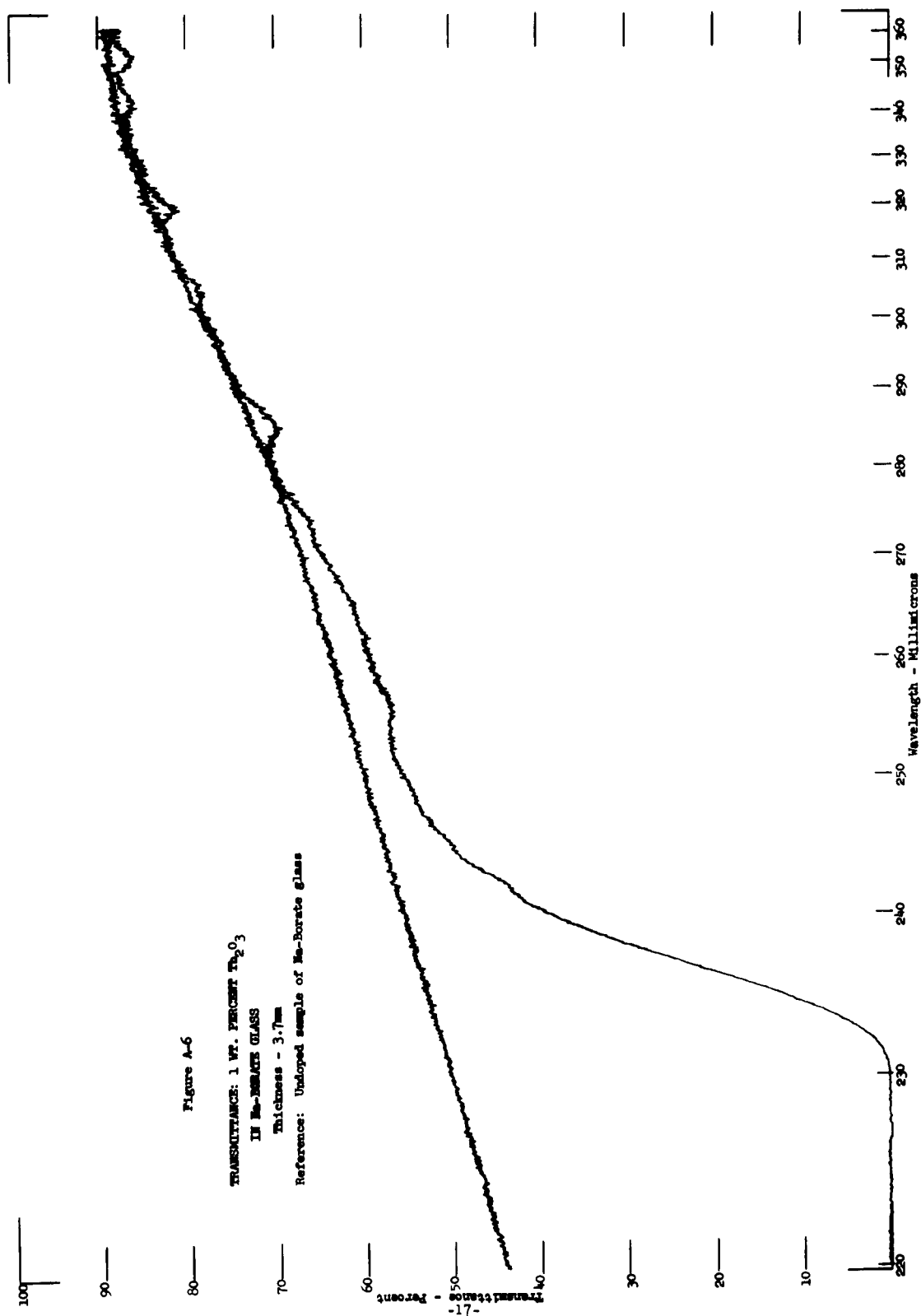












## B. Fluorescence Spectra

Exciting radiation from a tungsten lamp chopped mechanically at a 120 cycle rate was imaged on the neodymium and ytterbium glass samples for fluorescence emission measurements. The excitation for neodymium glass was filtered with 7mm of Pittsburgh No. 2043 heat absorbing glass and made incident at right angles to the optic axis of the spectrometer to reduce stray light. The filter could not be used for ytterbium since it absorbed the only available excitation wavelengths. Glass samples were held directly in front of the entrance slit of a Perkin-Elmer Model 83 monochromator. The combination of .05mm slits and LiF prism gave a spectral resolution of about 6 millimicrons. A lead sulfide detector, Welch Densichron amplifier, and Varian recorder were used to sense and record the fluorescence output.

Samarium fluorescence was excited by a mercury arc lamp and detected by a 7102 photomultiplier. Terbium fluorescence was excited by a Beckman hydrogen lamp and detected with a 1P21 photomultiplier.

The curves have not been normalized to an equal energy output so the data is strictly qualitative.

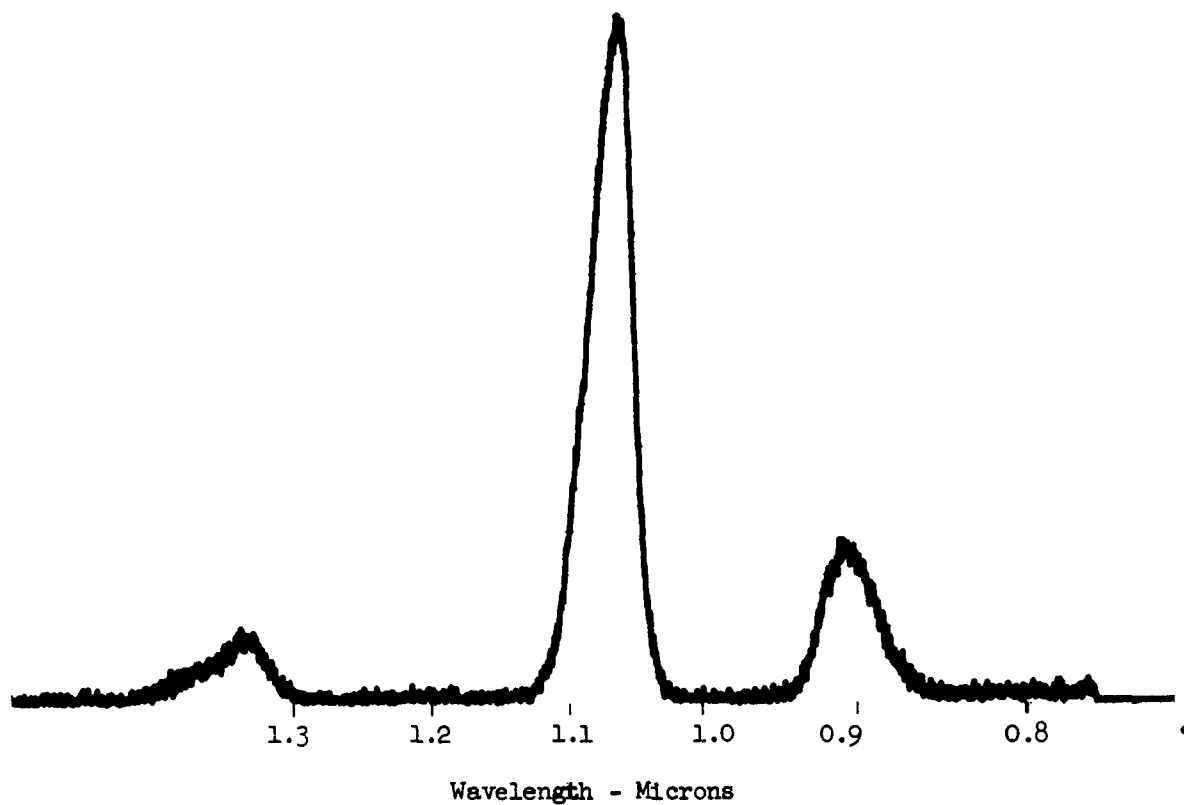


Figure B-1

FLUORESCENCE EMISSION FROM  
1 WT. PERCENT  $\text{Nd}_2\text{O}_3$  IN La-Ba-BORATE GLASS  
(Amplifier gain 4X that used for B-2 and B-3)

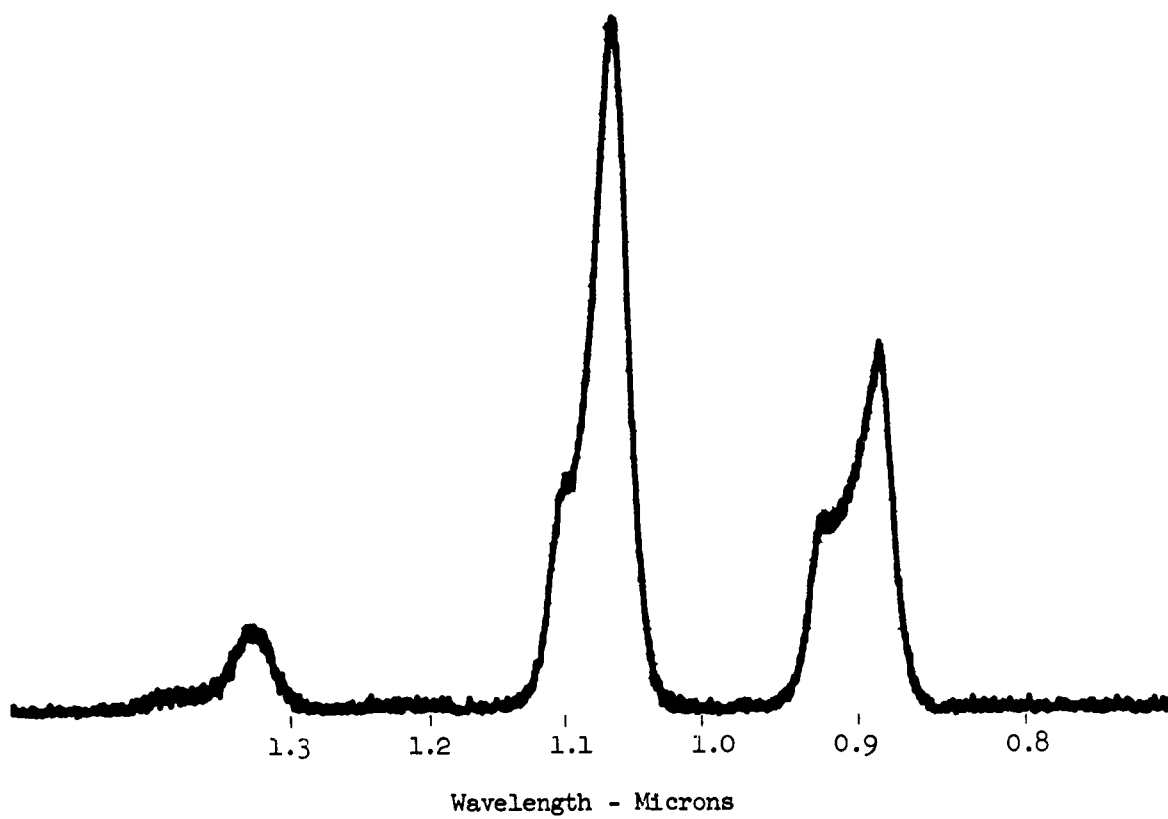


Figure B-2

FLUORESCENCE EMISSION FROM  
1 WT. PERCENT  $\text{Na}_2\text{O}_3$  IN <sup>K</sup>~~Na~~-Ba-SILICATE GLASS

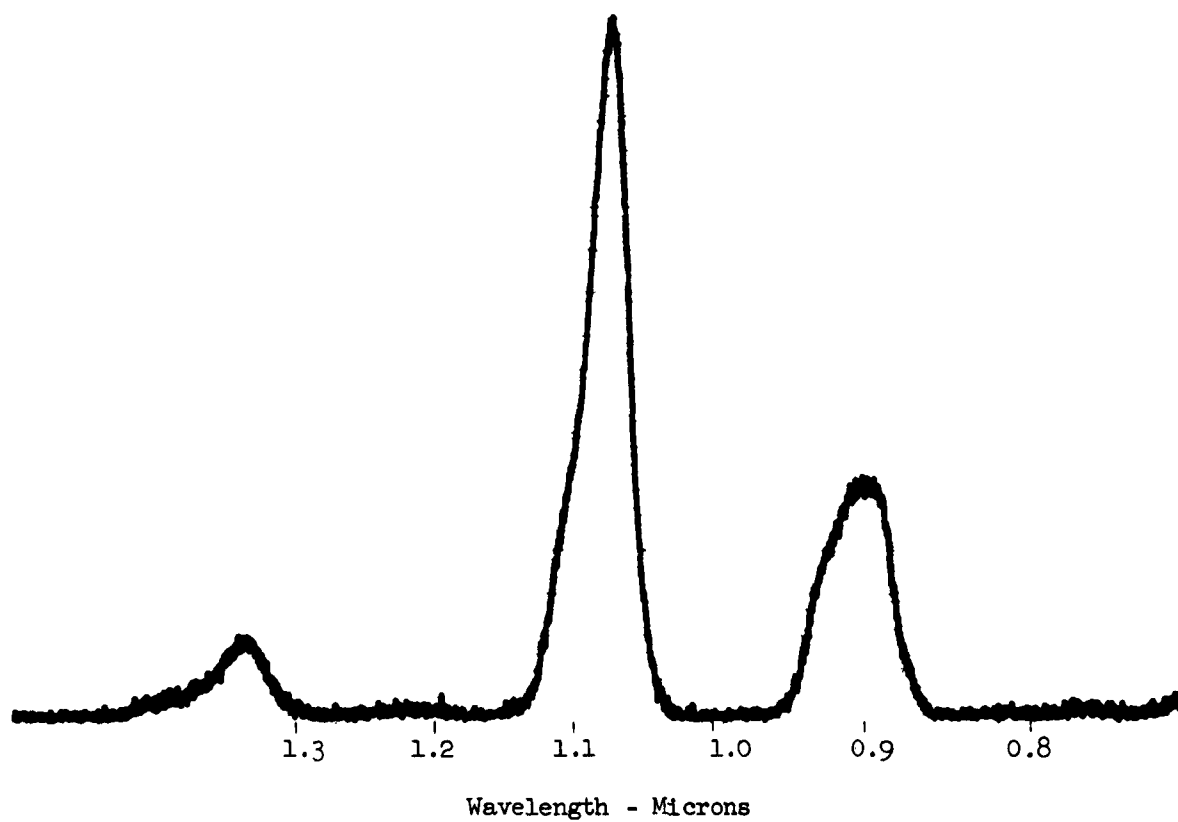


Figure B-3

FLUORESCENCE EMISSION FROM  
1 WT. PERCENT  $\text{Nd}_2\text{O}_3$  IN  $\text{La}$ -Ba-SILICATE GLASS

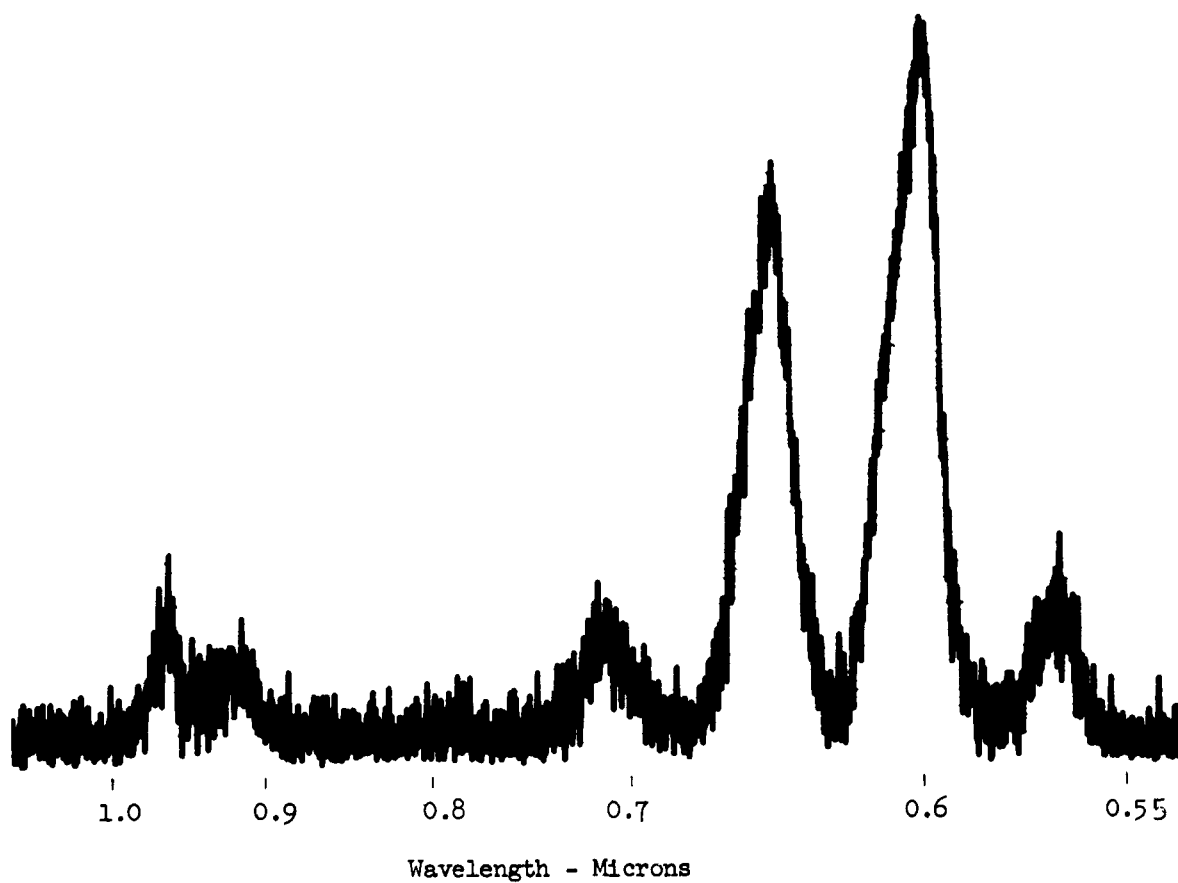


Figure B-4

FLUORESCENCE EMISSION FROM  
1 WT. PERCENT  $\text{Sm}_2\text{O}_3$  IN La-Ba-BORATE GLASS



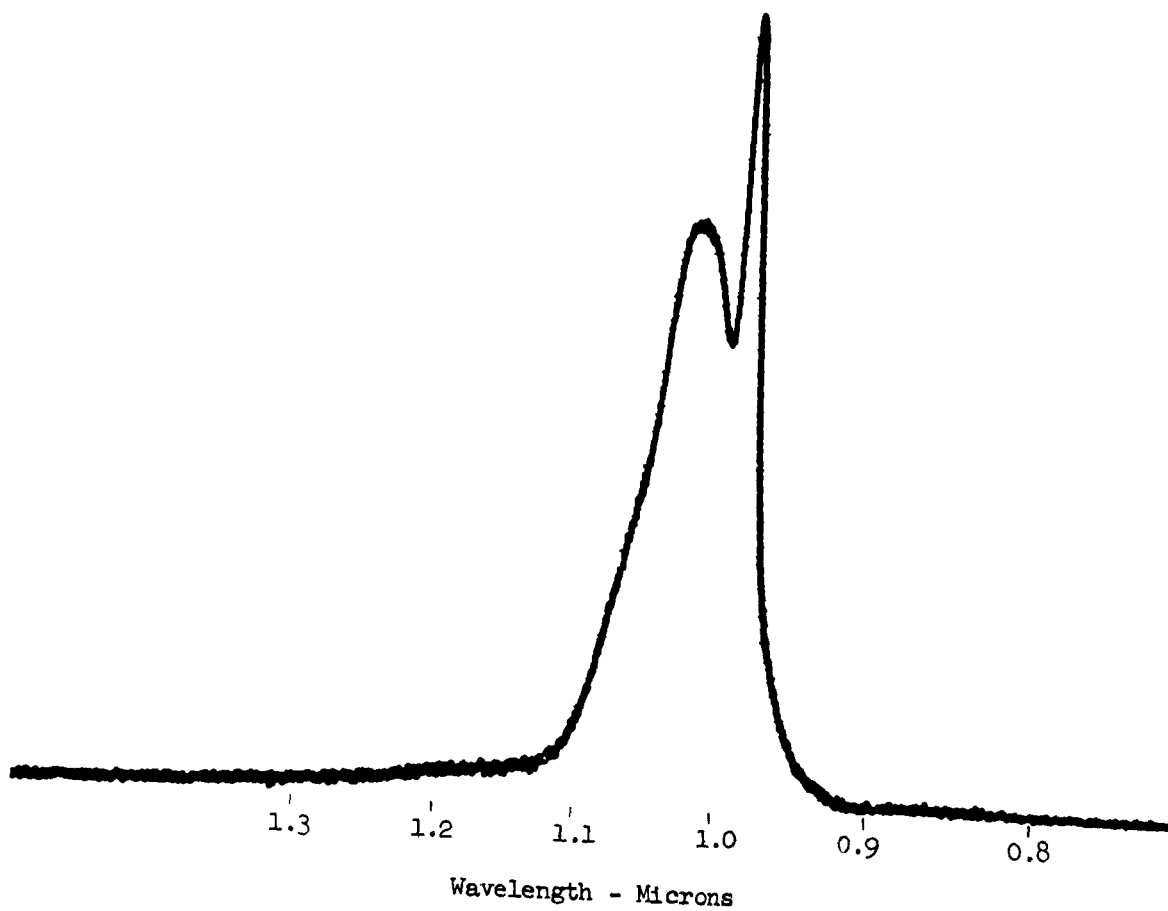


Figure B-5

FLUORESCENCE EMISSION FROM  
1/3 WT. PERCENT  $\text{Yb}_2\text{O}_3$  IN La-Ba-BORATE GLASS

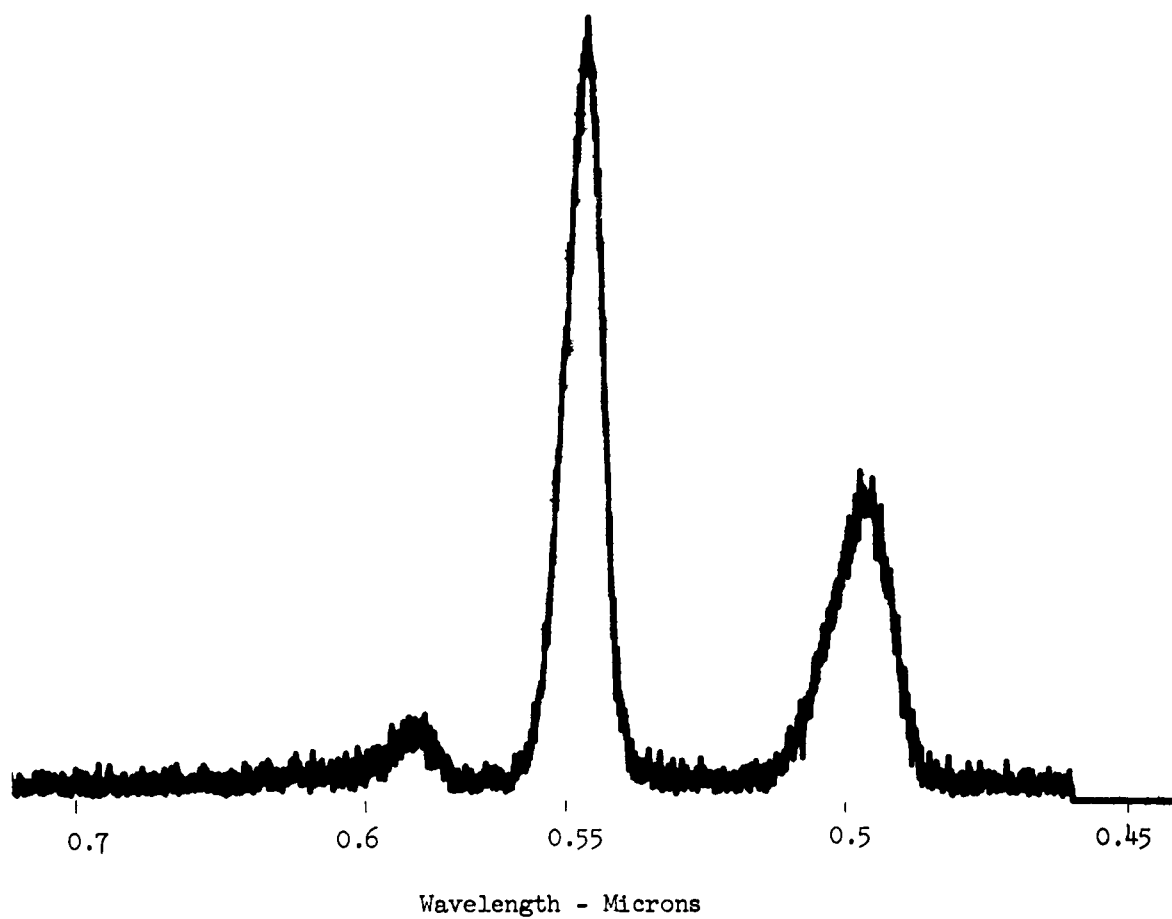


Figure B-6

FLUORESCENCE EMISSION FROM  
1 WT. PERCENT  $\text{Tb}_2\text{O}_3$  IN Na-BORATE GLASS

### C. Fluorescence Decay

Exciting radiation of about 4 microseconds duration from a Xenon flash tube was imaged on the glass samples. Detector output was observed with a camera-equipped Tektronix oscilloscope. The detector for neodymium fluorescence was a Hoffman EA7E1 silicon photocell, biased 0.5 volts, and covered by a 1/16" sheet of Rohm & Haas No. 2022 black plexiglass. The combination gave a wavelength sensitivity peak coincident with the 1.06 micron emission of neodymium. For the increased sensitivity needed to follow the decay for long times after excitation, a 7102 photomultiplier was substituted for the silicon cell. To minimize the effect of stray exciting light, the Xenon flash tube output was filtered with interference-type filters to remove wavelengths between 0.9 and 1.2 microns, and the detector aperture axis was at right angles to the incident exciting light.

Samarium and ytterbium fluorescence decays were detected by a 7102 photomultiplier without the plexiglass filter, and terbium fluorescence was detected by a 1P21 photomultiplier.

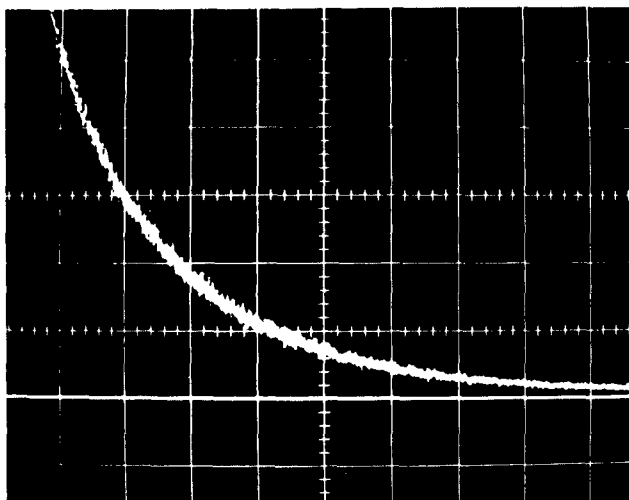


Figure C-1

FLUORESCENCE DECAY CURVE  
for 1/3 Wt. Percent  $\text{Sm}_2\text{O}_3$   
in La-Ba-Borate Glass  
1 Millisecond/Division

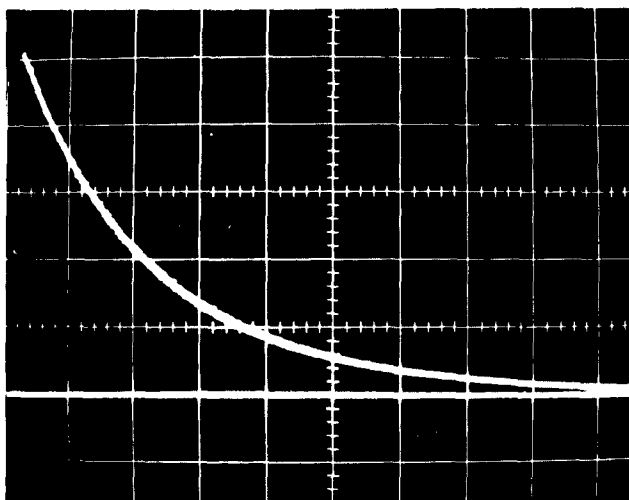


Figure C-2

FLUORESCENCE DECAY CURVE  
for 1/3 Wt. Percent  $\text{Yb}_2\text{O}_3$   
in La-Ba-Borate Glass  
0.5 Millisecond/Division

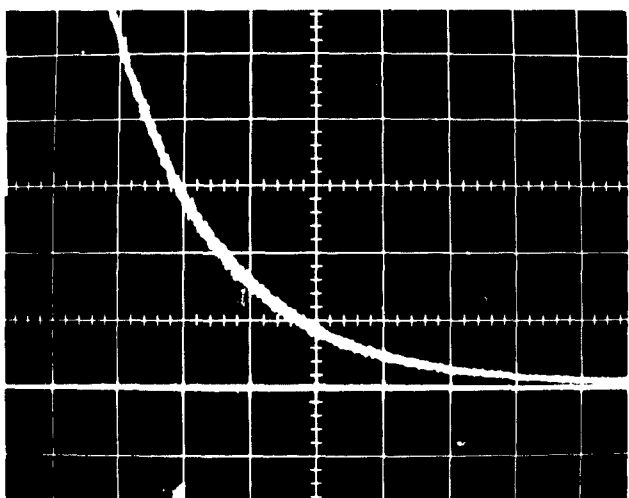


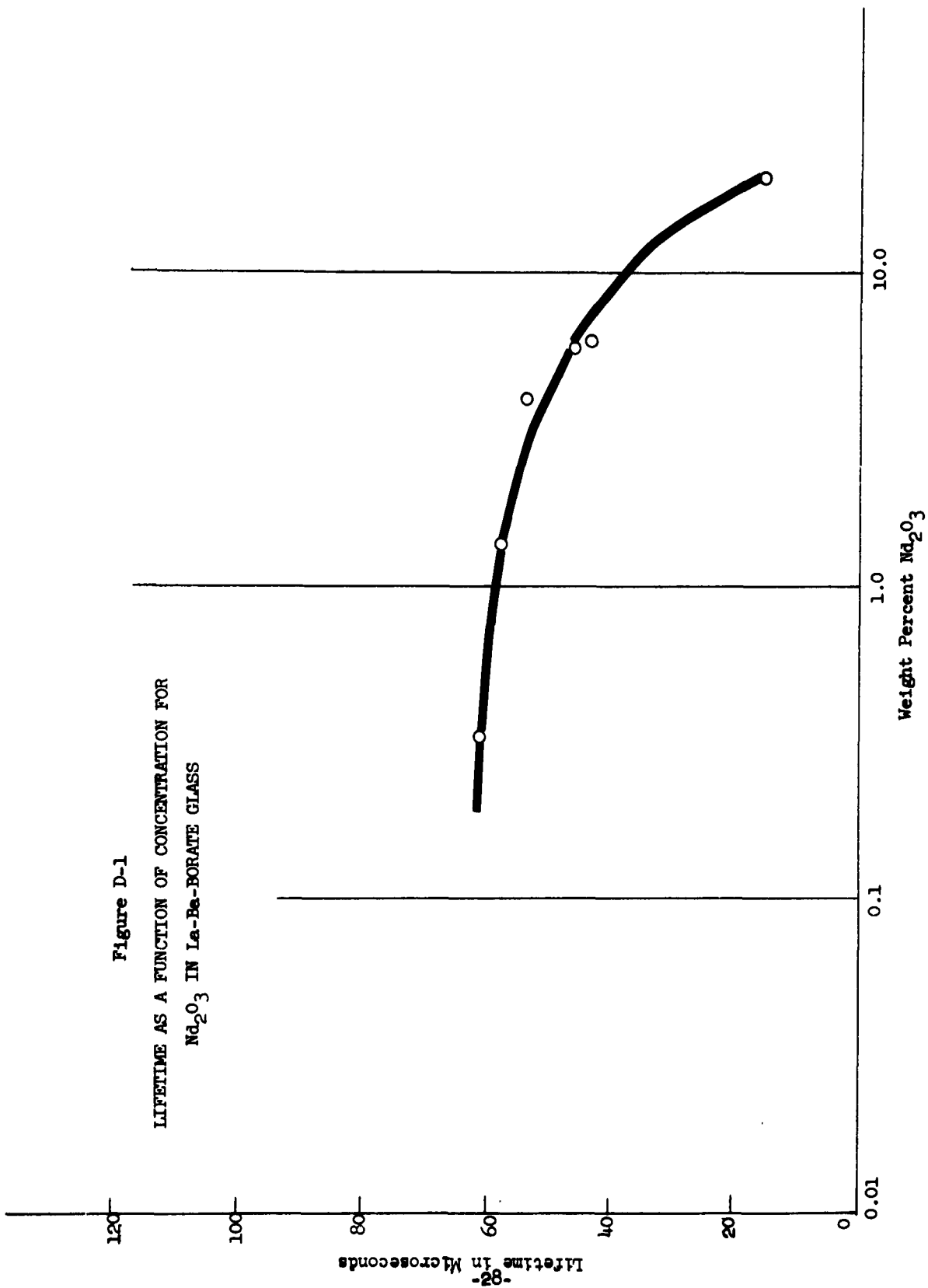
Figure C-3

FLUORESCENCE DECAY CURVE  
for 1 Wt. Percent  $\text{Tb}_2\text{O}_3$   
in Na-Borate Glass  
2 Milliseconds/Division

#### D. Decay vs. Concentration

Neodymium and samarium were investigated over a range of doping percentages to determine the influence of concentration on fluorescence. The data seem to indicate a greater influence of concentration on lifetime for samarium than for neodymium, at least in borate glass systems. This could be related to the longer lifetime of the samarium, and/or the tendency of the borate lattice to quench neodymium fluorescence. More data is needed on the effect of concentration in different glass bases.

Figure D-1  
LIFETIME AS A FUNCTION OF CONCENTRATION FOR  
 $\text{Nd}_2\text{O}_3$  IN La-BE-BORATE GLASS



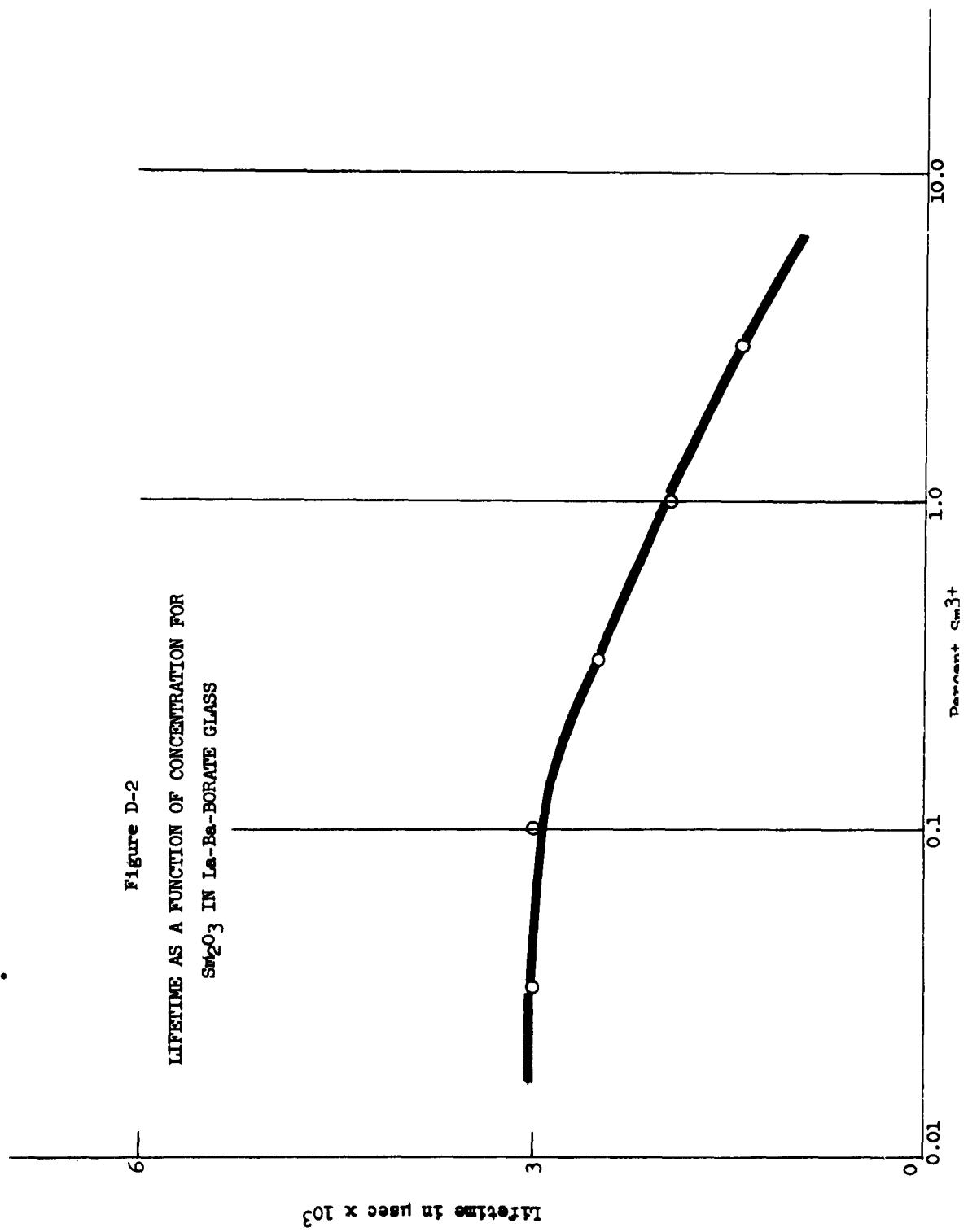


Figure D-2  
LIFETIME AS A FUNCTION OF CONCENTRATION FOR  
Sm<sub>2</sub>O<sub>3</sub> IN La-Ba-BORATE GLASS

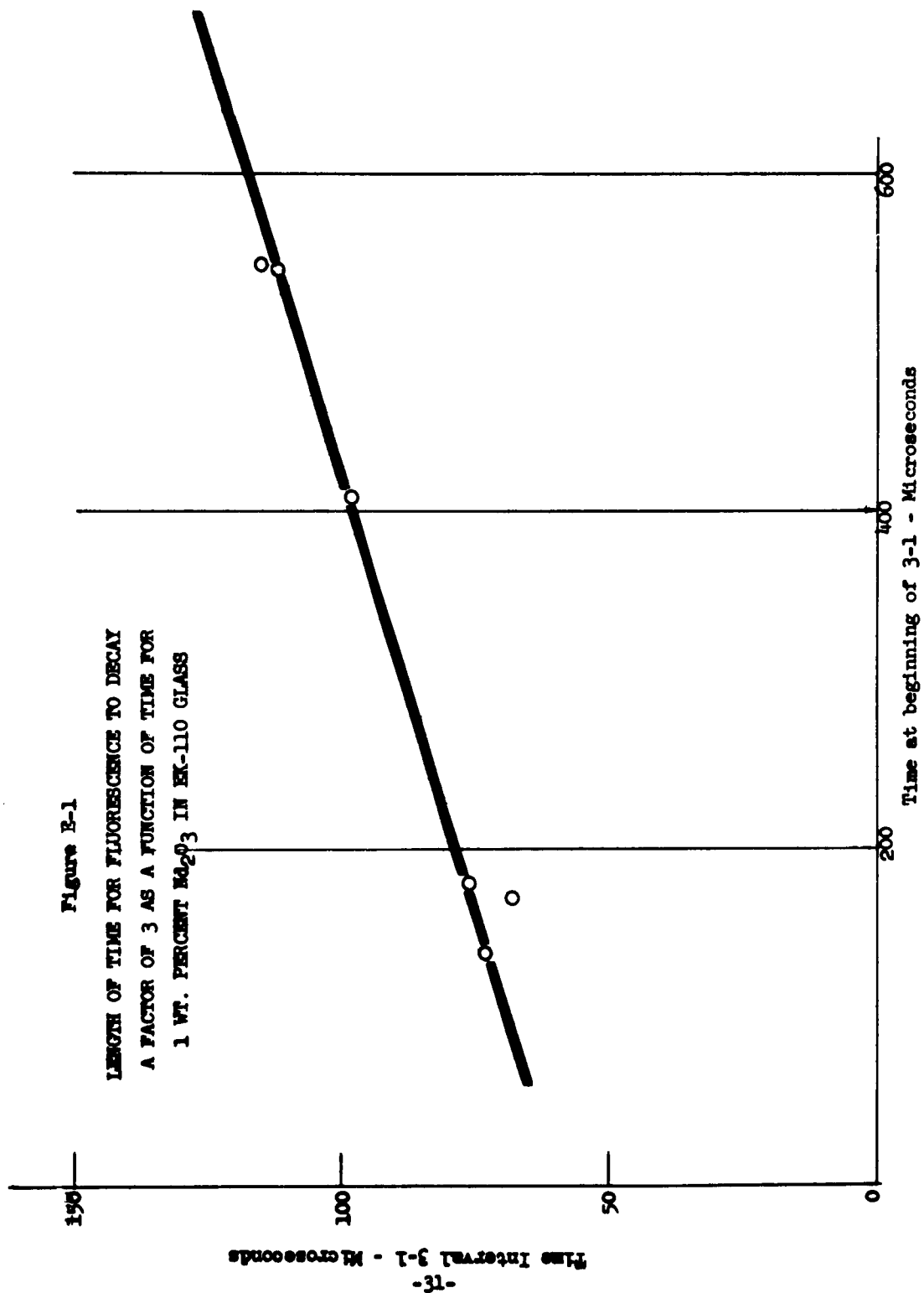
#### E. Decay vs. Time

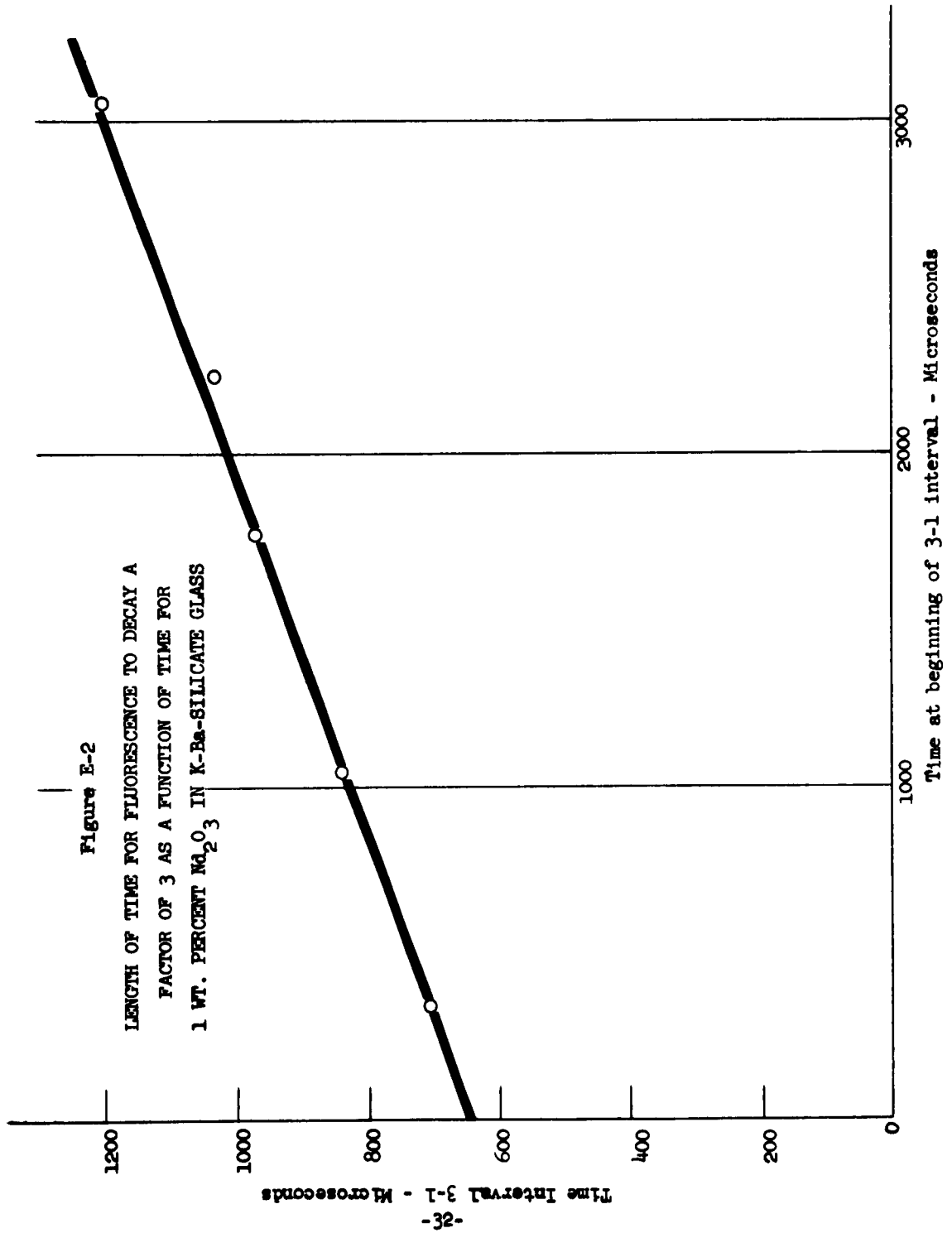
It was observed from the start of the fluorescence decay measurements that the curve did not follow an exponential law, and to define lifetime was a bit arbitrary. For the tabular data, we have chosen a portion of the curve about one "lifetime" after the excitation flash.

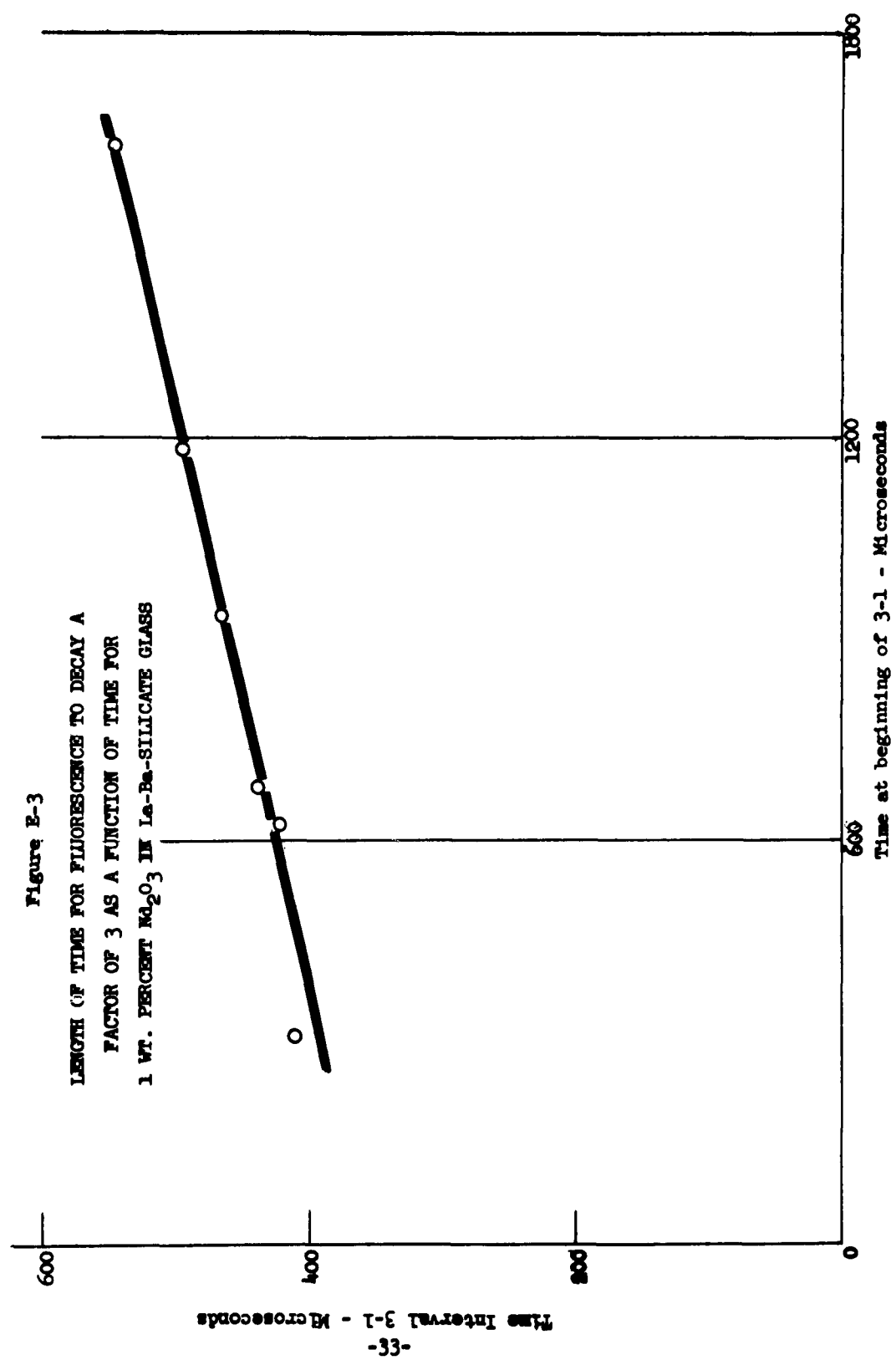
Through the use of a dual beam oscilloscope, we have observed the change of the character of the decay of fluorescence with time. A plot has been made of the time for the signal to decrease a factor of 3 as a function of the time after the initiation of the exciting flash.

Although non-exponential decays are usually thought of as being due to bi-molecular combination processes, the situation for rare-earth ions in glass is probably different. It may be associated with the slight differences in surround symmetry experienced by the individual ions.









## F. Laser Action

Due to the high temperature limitations of the furnace, only neodymium glass of high optical quality in borate systems has been fabricated. A sample of K-Ba-Silicate glass in laser rod form was purchased from another company. The fluorescence and absorption of this glass was similar to that of silicate glass previously made. Twyman-Green examination showed reasonable tolerances in the optical quality of the silicate rod.

Dielectric coatings of  $MgF_2$  and ZnS have been applied in the laboratory with considerable success as laser end coatings. Typically a 12-layer film is deposited on the highly reflecting end, and an 8-layer on the output end. The transmittances of these are 0.3 percent and 3.0 percent respectively. We have no good measurement of reflectance, but presume scattering loss to be of the order of 1 percent.

When identical coatings were applied to the silicate and borate laser rods, the threshold and power output were compared using the Electro-power-pacs exciter. The power supply condenser is rated at 200 mfd., 3000 volts maximum, and the flashtubes are 4 G.E. 91 types connected in series-parallel.

Typical values of threshold for laser action in 2 1/2" long, 1/4" diameter rods are 100 joules for borate glass and 400 joules for silicate. Since this is opposite to the effect one would predict from fluorescence efficiency and lifetime measurements, a suitable explanation was sought.

The possibility that quenching effects could be saturated at high excitation levels was considered. No lengthening of fluorescence lifetime was observed in borate glass by increasing excitation. The spiking of the laser output is characteristic of a shorter lifetime in the borate material. Silicate laser output appears to pulse and return to zero, whereas the borate seems to oscillate about a steady state value. The conclusion was that saturation of quenching plays a minor, if any, role in lowering the threshold of the borate glass. Further

substantiation was obtained by distributing inductors between the condensers in the power supply to create a lumped constant delay line. The resultant pump light was roughly constant for about 1.2 milliseconds. Silicate glass still required much more energy to reach threshold and the borate action started after about 600 microseconds of pumping.

One possible explanation would be an order of magnitude difference in low angle scattering between the borate and silicate glasses. Tittel (private communication) of General Electric in Syracuse, New York, has estimated the scattering loss in the borate glass to be less than 0.3 percent per centimeter. We have no data on silicate glass in this regard.

To investigate the ability of the borate glass to store energy, a simple Q-spoiling experiment has been performed. A 2-inch long  $1/4$  inch diameter, 3 percent Nd doped rod was coated for high reflection on one end and low on the other. A small prism was rotated at 3600 rpm in line with the low reflection coated end, and the output was observed through the high reflection end. The optimum activity appeared about 150 microseconds after the pumping light started, again illustrating the short lifetime of the borate glass.

Since the borate glass has a low threshold for laser action, the flash equipment was able to excite the material more than an order of magnitude above threshold. The output appears to increase quite linearly with input at all energies substantially above threshold. The maximum power output that was observed from a 3-inch long,  $1/4$  inch diameter rod is 2 joules. Chernoch (private communication) of General Electric in Schenectady, New York, has observed over 70 joules from a 12-inch long, 1 cm square rod of our borate glass. The output from this rod was limited to  $1/4$  of a degree cone angle.

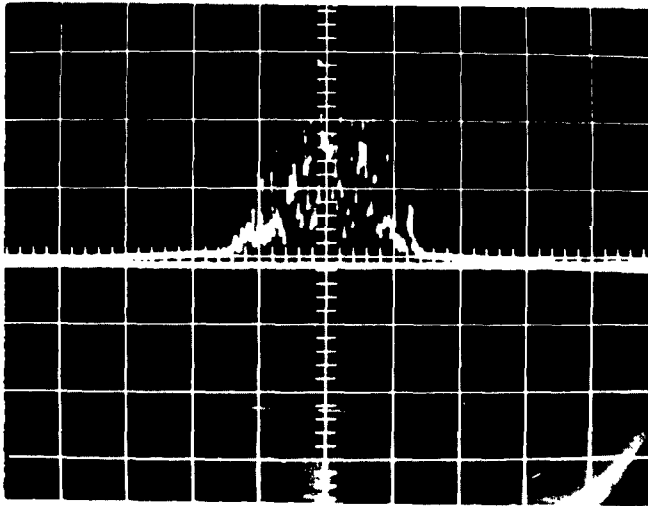


Figure F-1

Typical Nature of Laser Output  
As a Function of Time  
for 1 Wt. Percent  $\text{Nd}_2\text{O}_3$  in Borate G  
Time Scale 0.2 Millisecond/Division  
(Sweep right to left)  
Input power 144 joules

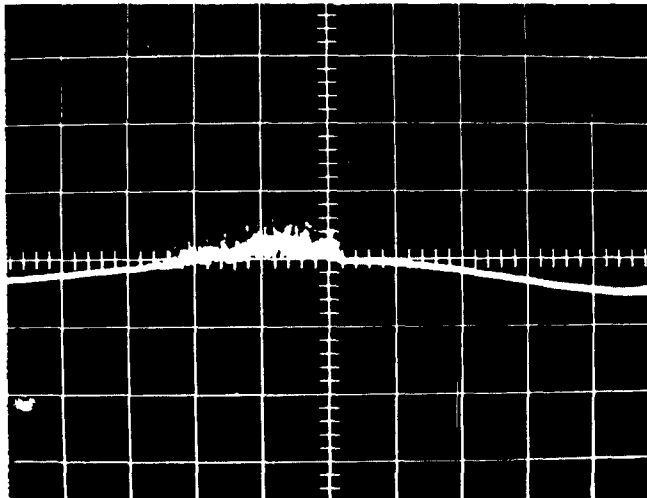


Figure F-2

Typical Nature of Laser Output  
As a Function of Time  
for 2 Wt. Percent  $\text{Nd}_2\text{O}_3$  in Silicate  
Time Scale 0.2 Millisecond/Division  
(Sweep right to left)  
Input power 530 joules

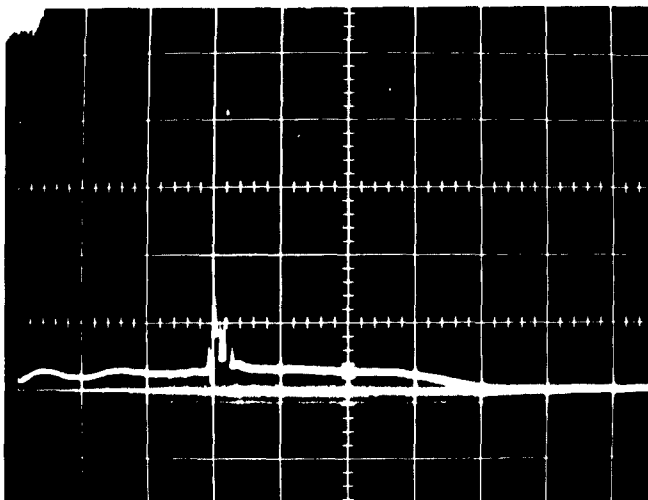


Figure F-3

Output near Threshold of Borate G  
with Constant Pump Light  
Time Scale 0.2 Millisecond/Division  
(Sweep left to right)  
Input power 196 joules

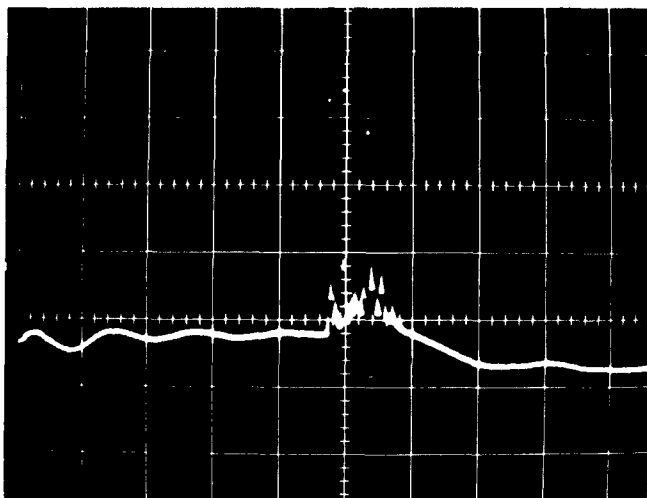


Figure F-4

Output near Threshold of Silicate Glass  
with Constant Pump Light  
Time Scale 0.2 Millisecond/Division  
(Sweep left to right)  
Input power 525 joules

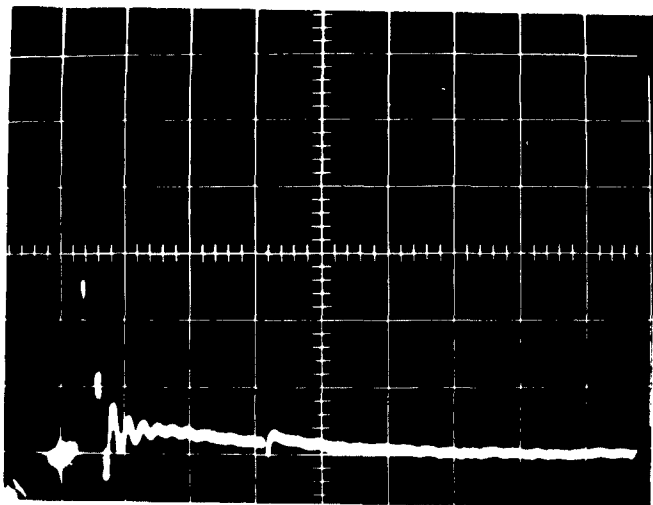
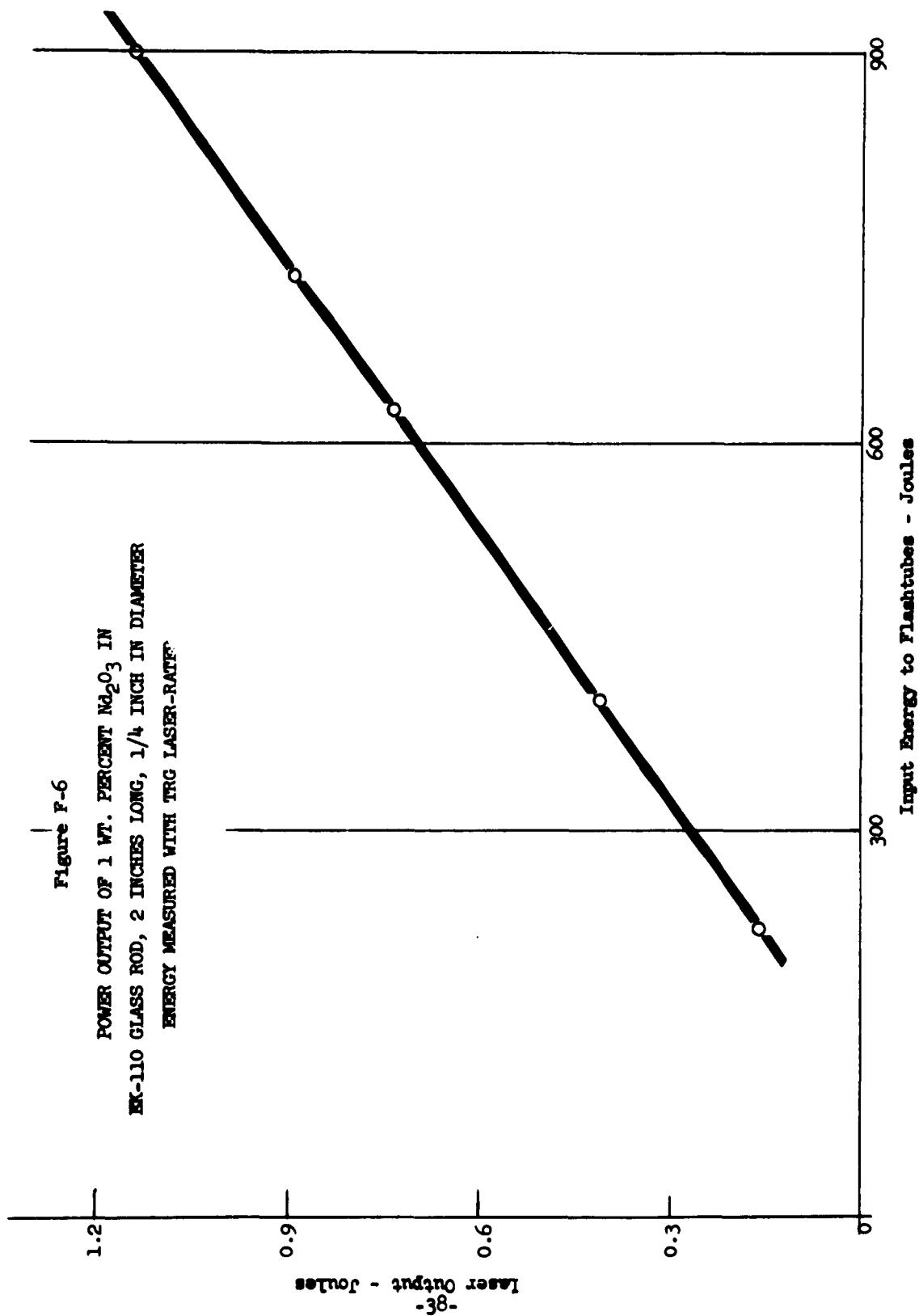


Figure F-5

Output of Q-spoiled  
3 Wt. Percent  $\text{Nd}_2\text{O}_3$  Ek-110 Glass  
Time Scale 50 Microseconds/Division  
(Sweep left to right)

(Oscillation near start of sweep  
due to pickup from flash trigger)





#### G. Absorption and Fluorescence Measurements on Various Glass Systems

We have prepared in tabular form a summary of the data taken from transmittance curves and fluorescence decay curves made using neodymium doped glass of various compositions. The glasses have been grouped according to their glass-forming constituent: boron, silicon or phosphorus.

The lifetime was derived from the photograph of an oscilloscope trace of the electrical output from a silicon solar cell-type photodiode. The glass fluorescence was activated by a flash of light, duration less than 10 microseconds, from a G.E. 230 flashtube. The activating light was filtered to remove wavelengths between 0.9 and 1.2 microns, and the photodiode was covered with a filter which removed all wavelengths short of 1.0 microns. In general, the observed exponential appeared non-linear, having a faster decay immediately following the exciting flash. The value presented in the table is the slower one observed near the end of the trace.

The absorption cross section for the 800 millimicron band was calculated from the peak observed absorption and the number of neodymium ions per cubic centimeter of material.

$$\text{if } I = I_0 E^{-\alpha X}$$

$$\text{then cross section} = \alpha / N$$

where  $I$  is the transmitted intensity of 800 millimicron radiation

$I_0$  is the initial intensity of 800 millimicron radiation

$X$  is the sample thickness in centimeters

$N$  is the number of neodymium ions per cubic centimeter

The absorption bandwidth for the 800 millimicron band is given in wave numbers, and represents the difference between the two wave numbers where  $\alpha$ , as defined above, has fallen to one half its peak value.

The relative absorption cross sections normalized to the absorption at 800 millimicrons for three other absorption bands are finally included to complete the table.

# BORATES

<u>GLASS NO.</u>	<u>Nd<sub>2</sub>O<sub>3</sub> Wt %</u>	<u>LIFETIME (μ sec.)</u>	<u>BAND WIDTH at 0.8μ ΔV/(cm<sup>-1</sup>)</u>	<u>ABSOLUTE ABSORPTION CROSS SECTION (cm<sup>2</sup>/ion X 10<sup>-20</sup> at 0.8μ)</u>	<u>RELATIVE ABSORPTION CROSS SECTION (based on 0.8 micron absorption)</u>		
					<u>0.680μ</u>	<u>0.742μ</u>	<u>0.880μ</u>
B-Ba 2186	20	15.4	320	1.685	0.067	0.743	0.248
B-La-Ba 2153	0.3	61.8	355	1.762	0.068	0.770	0.261
B-Ba-K 2201	1	58.5	334	1.582	0.070	0.732	0.251
B-La-Ba-Th 2174 n. ann.	1	70.0	305	1.994	0.090	0.755	0.264
2174 ann.	1	64.0	330	2.038	0.066	0.725	0.268
2180	1	67.0	335	2.437	0.074	0.753	0.254
2188R	6	46.0	312	1.900	0.061	0.747	0.248
2192	6	43.6	328	1.838	0.070	0.757	0.255
Ba-La-Ta-Th 2176	1	84.0	320	2.116	0.087	0.753	0.271
B-La-Ba-W-Th 2177	1	72.0	310	2.186	0.065	0.745	0.316
B-La-Ba-W-Zn-Zr-Al 2199	1	75.6	370	1.958	0.078	0.755	0.258
B-La-Ba-Si-Sr-Th 110-16258	3	54.0	330	1.835	0.071	0.781	0.278
B-Al-Pb-Zn-Ca-Zr 2175	1	58.2	314	1.734	0.072	0.830	0.261

# PHOSPHATES

GLASS NO.	$\text{Nd}_2\text{O}_3$ Wt %	LIFETIME ( $\mu$ sec.)	BAND WIDTH at $0.8\mu$ $\Delta\lambda/(\text{cm}^{-1})$	ABSOLUTE ABSORPTION CROSS SECTION ( $\text{cm}^2/\text{ion} \times 10^{-20}$ at $0.8\mu$ )	RELATIVE ABSORPTION CROSS SECTION (based on $0.8$ micron absorption)		
					$0.680\mu$	$0.742\mu$	$0.880\mu$
<u>P-Ia-Ba</u>							
2B in $\text{Al}_2\text{O}_3$	3	227.0	229.0	2.396	0.059	0.777	0.236
Vycor Crucible	3	173.0	219.2	2.246	0.057	0.779	0.237
4B Coors	3	132.0	213.0	1.720	0.068	1.039	0.296
Norton Sintered	3	264.0	272.0	1.746	0.071	0.909	0.306
Clean Platinum	0.3	300.0	227.0	3.411	0.056	0.787	0.246
<u>P-Al-Zn</u>							
2182	1	332.0	330.0	1.351	0.069	0.804	0.274

# SILICATES

GLASS NO.	Nd <sub>2</sub> O <sub>3</sub> Wt %	LIFETIME (μ Sec.)	BAND WIDTH at 0.8μ $\Delta \nu / (\text{cm}^{-1})$	ABSOLUTE ABSORPTION CROSS SECTION ( $\text{cm}^2 / \text{ion} \times 10^{-20}$ at 0.8μ)	RELATIVE ABSORPTION CROSS SECTION (based on 0.8 micron absorption)		
					0.680μ	0.742μ	0.880μ
<u>Si-La-Ba</u>							
2187	1	287.0	368	3.387	0.078	0.526	1.000 0.252
<u>Si-Ba-K-Sb (A O Type made by E.K.)</u>							
2179	3	681.0	381	0.501	0.082	0.948	1.000 0.353
2178	1	674.0	382	0.677	0.079	0.938	1.000 0.357
11B Vac Melted	1	646.0	380	0.707	0.070	0.936	1.000 0.332
<u>Si-Al-Mg-Li (NRL Type made by E.K.)</u>							
NRL	1	347.0	338	2.630	0.098	0.931	1.000 0.275
<u>Si-B-Sb-Zn-Ca-Mg-K (C-1 Crown made by B &amp; L, remelted by E.K.)</u>							
11R Vac Melted	1	414.0	275	1.130	0.076	0.732	1.000 0.331
15R Air Melted	1	521.0	243	1.174	0.076	0.816	1.000 0.317
8B Vac Melted	1	405.0	367	1.430	0.966	0.745	1.000 0.407

## H. Glass Optical Quality

There are two basic tools available for inspecting glass quality. One is the polariscope which indicates the presence of strain, and the other is the Twyman-Green interferometer which detects variations in refractive index.

The polariscope is insensitive to refractive index variations which influence both states of polarized light the same amount. It is used primarily as an indicator of the state of anneal of glass raw material and stresses introduced by local temperature variations. Its use does not require good optical surfaces, since surface refraction by homogeneous material is the same for both polarizations.

A typical standard for well annealed glass is that a maximum of 3 degrees phase displacement per centimeter thickness of glass is observed. An annealing cycle to produce this quality for an EK-110 glass less than one inch thick is as follows: Hold at 1150°F for 8 hours, cool 2° per hour to 1100°F, cool 3°F per hour to 1000°F, and return to room temperature at 5°F per hour. For material thicker than one inch, the initial temperature is held for 18 hours, and the cooling rates reduced to 40 percent of those for the thinner samples.

Other annealing hold temperatures and cycles will have to be worked out for newly developed glasses.

The Twyman-Green interferometer detects optical path differences as small as  $1/10$  wavelength of 546 millimicron light. This represents a sensitivity, for a 2-inch thick glass samples of refractive index 1.7, of one part index variation in  $1 \times 10^6$ . Photographs of the fringe pattern observed for three representative glass samples are included as Figures H-1, 2, and 3. The top picture shows 4 pieces of neodymium doped EK-110 type glass two inches thick. This quality is as good as any we have observed to date. The second photograph is more representative of EK-110, and illustrates the usefulness of the Twyman-Green in allowing good volumes of glass to be selected for finishing into laser rods.

The third photograph is another EK glass type EKF 497 which, though poor by comparison, is roughly comparable to good quality ruby and is better than any phosphate or silicate glass we have produced to date.

One weakness in our glass evaluation program is that neither the polariscope or the interferometer will detect small index variations with a high spacial fluctuation rate which occur uniformly throughout the material and tend to average out over long paths. These variations will scatter energy and may prove to be the basic limitation to the use of glass as a laser material. However, since single crystals with added impurities suffer similar problems, the best laser medium is yet to be determined.

TWYMAN-GREEN INTERFEROGRAMS



Figure H-1  
Ek-110 Glass with 1 Wt. Percent  $\text{Nd}_2\text{O}_3$   
2 Inches Thick



Figure H-2  
EK-110 Glass with 1 Wt. Percent  $\text{Nd}_2\text{O}_3$   
2 Inches Thick

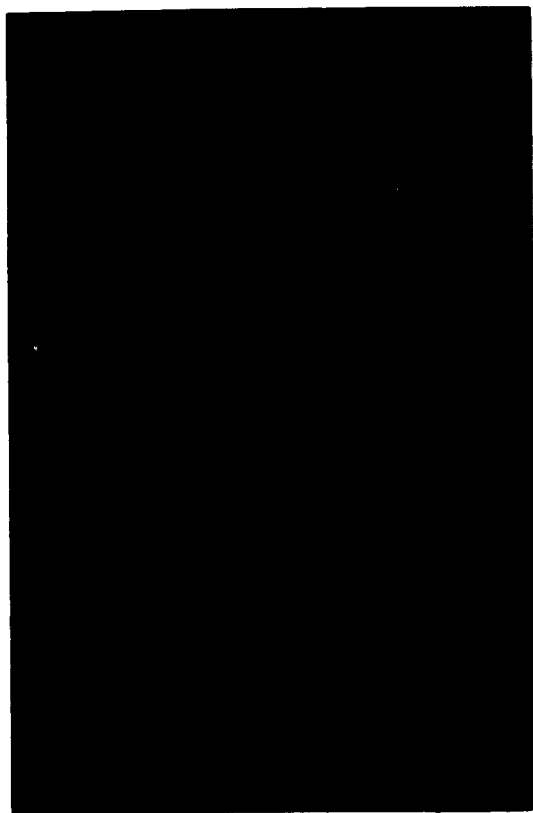


Figure H-3  
Ek-497 Glass with 1 Wt. Percent  $\text{Nd}_2\text{O}_3$   
2 Inches Thick

UNCLASSIFIED

UNCLASSIFIED